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16. ABSTRACT The report documents presentations at the Symposium on Iron and Steel Pollution Abatement Technology for 1981, Chicago, IL, October 6-8. The Symposium provided a forum for the exchange of information on technology problems related to air, water, and solid waste pollution abatement in the iron and steel industry. The opening session included presentations from EPA, the American Iron and Steel Institute, and Citizens for a Better Environment. The air session included papers on inhalable particulates, fugitive emission control, coke plant emission control, innovative air pollution technology, and iron and steelmaking emission control. Solid waste papers were on RCRA (the Resource Conservation and Recovery Act) and the steel industry, electric arc furnace dust recovery/recycle and treatment, and a panel on destruction of hazardous wastes in iron and steel furnaces. The water session included 14 papers on topics relating to water reuse/recycle, coke plant wastewater treatment, and new developments in wastewater treatment.

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a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Iron and Steel Industry Dust Wastes Processing Leakage Hazardous Materials Coking Water Pollution Waste Water Waste Treatment	Pollution Control Stationary Sources Inhalable Particulate Fugitive Emissions Solid Waste Biological Treatment Water Reuse/Recycle	13B 11F 11G 13H 14G

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PREFACE

These proceedings for the "Symposium on Iron and Steel Pollution Abatement for 1981" constitute the final report submitted to the Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency (IERL-EPA), Research Triangle Park, NC. The symposium was conducted at the McCormick Inn, Chicago, IL, October 6-8, 1981.

The opening session included a keynote address, presentations on the who, what, when, and where of environmental research in the iron and steel industry, and the air pollution of a steel mill from an environmentalist's viewpoint. Other sessions were conducted on air pollution abatement, covering inhalable particulates, fugitive emission control, coke plant emission control, innovative air pollution technology, and iron and steelmaking emission control; solid waste pollution abatement including a panel discussion on destruction of hazardous waste in iron and steel furnaces; and water pollution abatement, covering recycle/reuse of water, coke plant wastewater treatment, and new developments in wastewater treatment.

John S. Ruppersberger, Environmental Health Engineer, Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC, was Project Officer and General Chairman for the symposium.

Franklin A. Ayer, Manager, Conference Planning Office, Center for Technology Applications, Research Triangle Institute, Research Triangle Park, NC, was symposium coordinator and compiler of the proceedings.

TABLE OF CONTENTS

Page

OPENING SESSION 1
Richard D. Stern, Chairman

Opening Remarks 2
Richard D. Stern

Statement of Symposium Objectives 3
John S. Ruppersberger

Keynote Address 5
Carl J. Schafer

Whither Research? 8
E. F. Young, Jr.

The Unfinished Agenda: An Environmentalist's View of Steel Mill Air Pollution. 17
Kevin Greene

Session 1: AIR POLLUTION ABATEMENT 23
Philip X. Masciantonio, Chairman

INHALABLE PARTICULATES

Inhalable Particulate Matter Sampling Program for Iron and Steel: An Overview Progress Report. 24
R. C. McCrillis

FUGITIVE EMISSION CONTROL

Cost Effectiveness Evaluation of Road Dust Controls 39
Chatten Cowherd, Jr.,* Thomas A. Cuscino, Jr., and Mark Small

Blast Furnace Casthouse Control Technology - Fall 1981 Update 52
Thomas J. Maslany* and Peter D. Spawn

COKE PLANT EMISSION CONTROL

*Denotes Speaker

Page
Coke Quench Tower Emissions and Emissions Control 69
Dennis Wallace,* Naum T. Georgieff, Dana Peckworth, and Sandra Stell

Current Regulations and Control Performance for Visible Emissions from Wet-Coal Charging, Door Leaks, and Topside Leaks 87
Marvin R. Branscome* and William L. MacDowell

A Review of Shed and Gas Cleaning Systems for Controlling Coke Pushing Emissions from Coke Plants 103
Jack Shaughnessy* and Dilip Parikh

INNOVATIVE AIR POLLUTION TECHNOLOGY

Armco's Experience with Application of the Bubble Concept 111
B. A. Steiner

Engineering Study of Roof Mounted Electrostatic Precipitator (REP) for Fugitive Emission Control on Two Basic Oxygen Furnaces of 300 Ton Capacity. 120
Richard Jablin and David W. Coy*

Demonstration of the Use of Charged Fog in Controlling Fugitive Dust from a Coke Screening Operation at a Steel Mill. 139
Edward T. Brookman,* Kevin J. Kelley, and Robert C. McCrillis

IRON AND STEELMAKING EMISSION CONTROL

Performance of BOF Emission Control Systems 154
Leonard J. Goldman,* David W. Coy, James H. Turner, and John O. Copeland

Investigation of Opacity and Particulate Mass Concentrations from Hot Metal Operations 174
David S. Ensor

Retrofitting Emission Controls on Electric Furnaces at a Steel Mill 187
Michael P. Barkdoll* and Donald E. Baker

The Present and the Future for the Industrial Treatment of Fumes in the French Steel Industry. 202
Jacques Antoine,* Alain Milhau, and Jean Raguin

Modeling of Hood Control of Blast Furnace Casting Emissions . . .216
S. F. Fields,* C. K. Krishnakumar, and J. B. Koh

*Denotes Speaker

Page

Session 2: SOLID WASTE POLLUTION ABATEMENT 231
Thomas M. Barnes, Chairman
Robert S. Kaplan, Cochairman

RCRA Regulatory Changes and the Steel Industry. 232
Stephen A. Lingle* and William J. Kline

Characterization, Recovery and Recycling of Electric Arc Furnace Dust. 246
N. H. Keyser,* J. R. Porter, A. J. Valentino, M. P. Harmer, and J. I. Goldstein

Treatment of Carbon Steel Electric Furnace Flue Dust by Sulfation. 261
Pinakin C. Chaubal, Thomas J. O'Keefe, and Arthur E. Morris*

PANEL: DESTRUCTION OF HAZARDOUS WASTE IN IRON AND STEEL FURNACES. 279

Engineering Requirements for Thermal Destruction of Hazardous Waste in High Temperature Industrial Processes. 279
E. Timothy Oppelt

Suitability of Open Hearth Furnaces for Destruction of Hazardous Waste. 279
William F. Kemner

Suitability of Blast Furnaces for Destruction of Hazardous Waste. 280
George R. St. Pierre

Session 3: WATER POLLUTION ABATEMENT 281
Terry N. Oda, Chairman

RECYCLE/REUSE OF WATER

Minimizing Recycled Water Blowdown from Blast Furnace Gas Cleaning Systems. 282
Richard L. Nemeth* and Leonard D. Wisniewski

Minimizing Water Blowdowns from Selected Steel Plant Processes 300
Harold J. Kohlmann* and Harold Hofstein

*Denotes speaker

Page

Zinc Control in a Blast Furnace Gas Washwater Recirculation System. 307
R. Gregory Elder* and Roy Littlewood

Investigation of Reverse Osmosis for the Treatment of Recycled Blast-Furnace Scrubber Water. 320
M. E. Terril* and R. D. Neufeld

Review of Water Usage in the Iron and Steel Industry: Blast Furnace and Hot Forming Subcategories 344
Albert P. Becker, III, and Thomas M. Lachajczyk*

Control of Scale Formation in Steelplant Water Recycle Systems 362
G. R. St. Pierre* and A. H. Khan

Reduction of Wastes Discharged from Steel Mills in Metropolitan Chicago through Local Ordinance Enforcement. 373
Richard Lanyon* and Cecil Lue-Hing

A Mass Balance Model for Rinsewater in a Continuous Strip Halogen Electrolytic Tinning Operation for Use in Evaluating Wastewater Treatment and Recovery Alternatives. 388
James Skubak* and Ronald D. Neufeld

COKE PLANT WASTEWATER TREATMENT

Investigation of the Solid-Liquid Phase Separation of Preheated and Pipeline Charged Coke Battery Charging Liquor 403
S. R. Balajee,* A. I. Aktay, and R. R. Landreth

Assessment of the Biological Treatment of Coke-Plant Wastewaters with Addition of Powdered Activated Carbon (PAC) 424
Leon W. Wilson, Jr.,* Bernard A. Bucchianeri, and Kenneth D. Tracy

Biological Treatment of By-Product Coke Plant Wastewater for the Control of BAT Parameters 446
G. M. Wong-Chong* and S. C. Caruso

Two-Stage Biological Fluidized Bed Treatment of Coke Plant Wastewater for Nitrogen Control. 460
S. G. Nutt, H. Melcer,* and J. H. Pries

NEW DEVELOPMENTS IN WASTEWATER TREATMENT

*Denotes speaker

Page

Trace Metal Removal from Steel Plant Wastewaters Using Lime and Ferrate. 476
J. A. FitzPatrick,* J. Wang, and K. Davis

Pilot Evaluation of Alkaline Chlorination Alternatives for Blast Furnace Blowdown Treatment. 493
Stephen A. Hall,* Karl A. Brantner, John W. Kubarewicz, and Michael D. Sullivan

Closing Remarks 508
John S. Ruppersberger

UNPRESENTED PAPERS. 509

Application of Second Generation Chemical Solidification/Fixation Processes to Iron and Steel Hazardous Waste Problems. 510
Jesse R. Conner

Optimizing Existing Wastewater Treatment Facilities in Preparation of Meeting BAT/BCT Regulations in the Iron and Steel Industry 525
Meint Olthof

Development of a Deoiling Process for Recycling Millscale 536
Derek S. Harold

Recycling of Tar Decanter Sludge. 543
R. B. Howchin and M. S. Greenfield

APPENDIX: ATTENDEES. 546

*Denotes speaker

OPENING SESSION

Chairman: Richard D. Stern
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC

OPENING REMARKS

Richard D. Stern
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC

Good morning and welcome to the third symposium on Iron and Steel Pollution Abatement Technology. My name is Richard Stern and I am Chief of the Industrial Processes Branch at EPA's Industrial Environmental Research Laboratory at Research Triangle Park, North Carolina.

I am particularly pleased to welcome you all this morning since I am relatively new in this industry. About six months ago the Laboratory underwent a reorganization and the ferrous metallurgical industry, including iron and steel, was transferred into my area of responsibility. Norm Plaks, who headed up the branch previously, was transferred into Chief of the Particulate Technology Branch and is sorry he could not be here. However, he sends his regards to the friends and colleagues that he has acquired over the thirteen years he has worked with you in this industry.

Although I have only been involved with the industry a short time, I have been impressed and encouraged by the cooperation I have seen between us in the EPA's research and development program and you in the iron and steel industry. I have met a number of you these last few months, and I am looking forward to meeting many more of you during this symposium and possibly working with some of you on potential future cooperative projects. Regarding those projects, close coordination to select and focus on key areas of effort will be imperative. In view of declining resources, we will all have to zero in on very select, high-priority projects. I am looking forward to meeting many of you in the next few days and working with you.

Now I would like to introduce your Symposium Chairman, John Ruppersberger.

STATEMENT OF SYMPOSIUM OBJECTIVES

John S. Ruppersberger
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC

I would like to add my welcome to this, the third symposium on Iron and Steel Pollution Abatement, sponsored by EPA's Industrial Environmental Research Laboratory at the Research Triangle Park. The symposium provides a forum for the exchange of information on iron and steel multi-media pollution abatement technology. This symposium continues as a high priority activity due primarily to the opportunity it provides for learning and the cooperation encouraged by gathering members of industry, government, research and engineering organizations, universities, associations, control equipment designers and vendors, and others interested in pollution abatement for the iron and steel industry. The symposium provides an opportunity to learn, not only from what is presented by the speakers, but from questions and other discussions. We need to learn from each other. The results can be better solutions to pollution abatement problems. These solutions can take the form of more efficient and cost-effective technology, more productive research and engineering, and improved equipment design and operation.

This is an EPA office of research and development symposium, only to the extent that we have sponsored it, and we have worked to make it happen. This year only about one-fourth of the papers are from work funded by EPA-ORD. Our prime function is to serve as a catalyst. We seek to provide better information; that is, not just more information, but rather more accurate, more pertinent, and more practical information in a well-engineered sense. It is good to have greater participation in this symposium from others, especially from industry, due to the simple fact that any real achievements in pollution abatement are accomplished there.

After the opening session, the papers are grouped by media--air, solid waste, and water. Solid waste is getting more emphasis this year to reflect its increased importance. Many of the papers are actually multi-media, but were placed in the media of principal concern. Several of these papers contain the broader perspective of multi-media impacts that is essential in achieving effective pollution abatement technology.

This is an open forum--we encourage your active participation and a variety of viewports. Time for questions has been scheduled at the end of each paper. However, since this is a technical symposium, please save any non-technical questions and discussions for breaks and other times. The papers represent the views of their authors. They do not represent EPA policy. Please ask your questions--they contribute much to the symposium. We are here to learn from each other. I welcome you all and hope you benefit from and enjoy this symposium.

KEYNOTE ADDRESS

Carl J. Schafer
Industrial and Extractive Processes Division
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Washington, DC

As befits one from Washington, DC, nowadays, I think I should probably keep my own remarks brief in deference to Earl and Kevin, who I think probably have more to say than I do. The fact that this is the third symposium on Iron and Steel Pollution Abatement Technology, that we have been working together that many years, that we have got that much research going on to report on, is significant in its own right. It occurred to me to look back at some of the people and some of the projects that we have been involved in as I was thinking about the theme that we might adopt for this third symposium on pollution abatement in the iron and steel industry.

Our cooperative efforts began more than a decade ago. Several projects were initiated in the late 60's; for example, combined treatment of steel mill and municipal wastewater which is, of course, now common practice in several areas of the United States and, especially, right here in Chicago, was studied with National Steel Corporation with the help of Bill Smith of that company. Countercurrent rinsing on the halogen tin plate line at National Steel Corporation's Weirton Plant demonstrated the large blowdown reduction and accompanying economic benefit derived by recovery of the tin previously lost to the system. More recent cooperative efforts include several projects to encourage increased process water reuse/recycle. One study is of low cost modifications for blowdown reductions. The efforts of Don Lang at Inland Steel and Bob Peterson at U.S. Steel, Baytown, are stated in this study. Other work, of course, involves our mobile wastewater treatment trailer which is currently at Republic Steel in Cleveland on blast furnaces 5 and 6. Dick Nemeth and Len Wisniewski of Republic Steel will present a paper on this project later on in the session about the opportunities to significantly reduce blowdown. The air portion of our program with the iron and steel industry has also relied on cooperative projects, beginning in 1970 with the initiation of the Jones and Laughlin Pittsburgh work, P-4 battery, coke oven charging demonstration. In this project we worked, of course, with Earle Young. The project served as a proving ground for many innovative technologies, some of which are in common use today.

Another more recent EPA/AISI project coordinated with the AISI Coke Practice Committee under Don Gregg concerned the development and demonstration of improved coke oven door seals. Major field work was done with Jim McCord at Bethlehem's Lackawanna works and with Lloyd Hoopes at

Republic, Youngstown. Most current projects depend on industry cooperation in the form of providing access to facilities for the purpose of emission quantification and to support these activities through installation of sampling facilities, etc. A good example here is the work Murray Greenfield of Dominion Foundries and Steel Company on inhalable particulate emissions. The work there was in a cast house and the coke quench tower. Armco's support of similar tests of open source BOF and electric arc furnace emissions at three of their plants is another example of EPA/industry cooperation. Bruce Steiner of Armco will be presenting a paper on this work this afternoon as well.

A significant area of cooperation between EPA and AISI is through our activities involving the American Iron and Steel Institute. In the past we have enjoyed an excellent relationship through Bill Benzer and we are continuing that relationship today in the same spirit with Steve Schwartz. The AISI organizes several committees composed of members from corporations that belong to AISI to meet with the EPA personnel to coordinate major program areas and work together on specific projects. The AISI and the EPA have cosponsored several research projects at various universities. Particularly satisfying is the support that we have received from AISI on our program with other nations, especially the Soviet Union where we have an active exchange program on iron and steel technology. Over the past seven years, we have been fortunate to have industry experts such as Bill Benzer and Len Wisniewski as members of the team during visits to the Soviet Union. AISI and many member companies, including U.S. Steel, National Steel, and Inland Steel, have served as gracious hosts during visits of Soviet specialists to the United States. The information exchange was mutually beneficial to both sides.

There are many opportunities now to develop better solutions to the problems that we are all aware of. The need for more secure handling and disposal of hazardous waste has spurred renewed emphasis on prevention, recovery, or other more cost-effective alternatives to disposal. Often these alternatives to disposal include more effective utilization of resources or resource recovery. These alternatives seek to be more cost effective. They may produce a profit. These alternatives are not only good environmental solutions, they are good business. The AISI Task Force on Solid Waste, as well as ourselves, have listed several projects of mutual interest, but also projects which promise mutual benefit. Many of these projects are in the area of solid waste. Especially, I would like to note that the solid waste session of this symposium does include a paper on electric arc furnace dust, one of the AISI Task Force initiated projects. This project is of a special interest because the AISI working through its member companies, through agencies of the U.S. Government, surveyed the range of areas available and identified this particular project as being the one of particularly high potential for a payoff that would benefit the companies and, if we make it work, would benefit the environment through the alleviation of this solid waste disposal problem. Of course, the other media--air and water--also include opportunities for developing mutually beneficial cost-effective technology. These include the charged fogger paper which you will hear in the air session and the water reuse/recycle papers in the water session. One of our recently completed wastewater studies involved meetings with foreign steel plants and regulatory personnel of ten foreign governments from all over the world. One thing noted by our participants in these meetings was a spirit of cooperation between the industry and the government. The industry seemed willing to openly discuss its pollution problems and the government seemed willing to work toward national, well-engineered solutions to these problems. This spirit of cooperation between industry and government is one that we have enjoyed and that we wish to continue to engender through symposia such as this and other cooperative programs. There is a lot yet to be done; we have many opportunities. Technical people working together to achieve technical solutions can achieve the critical mass necessary to solve these problems reasonably balancing environmental concerns with our economic resources. The name of the game is, as it has been, cooperation. Reviewing the history, then, we have seen plenty of that cooperation. This cooperation now is not so much an institutional, dry, bureaucratic cooperation as it is the cooperation of people working together. Just in naming a few of the people with the steel companies that have been working on these projects with our own people brings this sharply to mind. The conference is a forum for those people who are working on individual projects who may not have the opportunity to know of the other projects, to crossfertilize each other. The forum is one to engender increased cooperation, increased technical excellence, increased technological solutions to problems. Let us keynote for this symposium then the cooperation and working together between EPA and a revitalized iron and steel industry as we go ahead.

Thank you very much.

WHITHER RESEARCH?

by: E. F. Young, Jr.
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ABSTRACT

This paper reviews the WHO, WHAT, WHEN, and WHERE of environmental research in the iron and steel industry, and makes projections and suggestions as to future conduct of research in the field.

It is a real pleasure to be one of the lead-off speakers at the third annual symposium on Iron and Steel Pollution Abatement Technology. I began, at the first of these symposia, with a review of the many different lines of technology development--research, development, and demonstration--on pollution control in the iron and steel industry. Now that the third symposium is here, I would like to take an overall look at what we have done, where we are, where we are going, and where we should be going. And when I say "we," I mean all of us, EPA, industry, academia, and independent consultants and researchers. We are all working toward the common goal of an improved environment. And we all have to recognize that achieving that improved environment is a matter not just of technology but also of dollars and cents. With that thought in mind, I would like to review what has been covered in past symposia and is being covered in this one. I would like to look for trends and to project where we should be going in the future.

As a first step in trying to analyze where we have been and where we are going, I took a look at the subject matter (Table 1) of the papers from these first three symposia. In 1979 50% of the papers dealt with air,

TABLE 1. SUBJECT MATTER

	Percentage		
	1979	1980	1981
Air	50	42	38
Water	25	39	33
Solid Waste	21	13	17
Multimedia	4	6	12

25% with water, 21% with solid waste, and a mere 4% with what I call multimedia assessment. In 1980 papers on air pollution control dropped off to 42%, water pollution control was up to 39%, solid waste dropped to 13%, and multimedia studies were up a little at 6%. This year's program involves 38% on air pollution, 33% on water pollution, 17% on solid waste, and 12% on what I consider multimedia analysis. One conclusion that could be drawn from this table is that it simply represents what papers were available for presentation in a given year. Another would be that the planners of the program had attempted to organize it a little differently. But I think there is something a little deeper to be drawn from this analysis, and I hope a guideline for the future; that is, the growth of multimedia papers. We tend all too often to look at narrow problems in isolation and yet, as time goes on, we realize more and more that, in cleaning up the water, we tend to produce solid wastes which must be disposed of. And in disposing of solid wastes, we run into the danger of contaminating both air and water. Since the real goal of our efforts is not just to achieve clean air and not just to purify water but to assure an improved overall environment for man, it seems to me that we need more analyses which consider all aspects of the actions that we take. We need more work which considers not a single medium but the overall impact of various control actions on all aspects of the environment. I think the little trend chart we have here shows that we have started giving more consideration to overall environmental impacts, and I hope that this presages more analyses of this type and more looking at the overall environment in the future.

The next question I asked myself was, who has been doing the work? So, again, I reviewed the three symposia to date (Table 2) and I found that the first was very much dominated by EPA and its contractors. Between

TABLE 2. SOURCE OF PAPERS

	Percentage		
	1979	1980	1981
EPA	9	10	2
EPA Contractor	58	41	37
Steel Company	22	26	31
Joint	4	10	9
Other	9	13	21

them, they gave 67% of the papers. That dropped off in subsequent years to 51% at the second and 39% at the third. The steel companies themselves presented 22% of the papers at the first, 26% at the second, and 31% at the third. Joint research between EPA and the industry accounted for only 4% of the papers at the first, 10% at the second, and 9% at the third. Papers from other sources went from 9% at the first to 21% in the current symposium. What is significant here? EPA domination of the first symposium was to be anticipated, I think, since EPA set the symposium up, and pulling the first one together was a big job. So, they had to rely on themselves and their contractors. That first meeting was a success, so papers from other sources have poured in, and EPA has proportionately cut back its domination. Industry has increased the number of papers it is presenting here. I do not think that this is an indication of increasing work on the part of the companies, but rather increasing recognition that this symposium is an important place to present the work. Jointly-sponsored work between industry and EPA has increased but still represents a rather modest proportion of the papers presented. And others have increased significantly. Who are these others? Some are guests from other countries, and I think this is a very sound and good development: the problems of pollution control are problems of the world, not just of this country; it is highly desirable to have an international flavor to these symposia. And others represent work by contractors who have seen opportunities and markets in the steel industry and are using this as an opportunity to present the sort of technical information that can permit their work to be evaluated.

There is one thing these particular statistics do not show, however, that I think is important. These statistics show only a small proportion of the papers represent joint work between EPA and the steel industry. In reality, however, there is a great deal of cooperation between the industry and the Agency. I think this cooperation is essential and should be stressed to a greater extent.

When EPA selects a contractor and puts him to work on a study of some aspect of our industry, that study cannot properly be done in isolation. EPA recognizes this and in almost every case, once a contractor has been selected for a significant study of the steel industry, EPA has approached the American Iron and Steel Institute and asked for our technical assistance in carrying out the project. This is normally followed up by a meeting among EPA, the contractor, and AISI technical people to discuss the project prior to its inception. During the conduct of the project, occasionally there are progress meetings. Then, as reports are prepared, AISI will work with the contractor and EPA on the assembly of a final report. AISI's advice and comments are, of course, not binding on EPA or its contractor, nor are they meant to be. This is a case of technical cooperation between the industry and the Agency.

I believe that this voluntary technical cooperation is of great advantage to all parties involved. The industry is much more likely to agree with results of the studies when we have had an opportunity to make input as that study develops. The contractor is much less likely to start down unproductive lines when he has the direct technical input of the industry experts most familiar with the operations. The Agency then gets a better work product as a result.

My next effort at analyzing where we have been consisted of classifying the papers by types (Table 3). I think I should emphasize at this

TABLE 3. TYPES OF PAPERS

	Percentage		
	1979	1980	1981
Regulatory Analyses	12	6	11
Technical Review	12	13	14
Quantification of Emissions & Effluents	22	10	8
Laboratory Conceptual Studies	8	30	31
Pilot Studies	17	16	19
Demonstration	17	19	17
Environmental Assessments	8	6	
Cost/Effectiveness/Cost/Benefit Analyses	4		

point that this is a totally arbitrary breakdown based solely on my thinking. You might not agree with the categories I have established; you might not agree with what categories I have placed some papers in. Nonetheless, I hope I have been able to come up with some useful analysis.

I set up a number of categories: Regulatory Analysis, Technical Review, Quantification of Emissions and Effluents, Laboratory and Conceptual Studies, Pilot Studies, Demonstrations, Environmental Assessments, and Cost/Effectiveness/Cost/Benefit Analyses. Before I discuss what the statistics or trends are in these categories, perhaps I should explain what is meant by each category and maybe give you some examples of papers in each.

The first is Regulatory Analyses. Since the nation's regulatory programs determine so much of what is required in the area of pollution control, an essential part of the background of any thorough look at research is an analysis of the regulations and what is required under them. Papers fitting in this category would be typified by one of the first papers in the first symposium, Don Goodwin's presentation, "Air Pollution Emission Standards." A more recent example would be the paper being given tomorrow on "Impact of RCRA on Solid Waste from the Steel Industry." I think these papers are invaluable in that it is the regulatory programs that guide the nation's environmental control program. Thus, the technology needed is a function of these regulatory analyses.

The next category I set up was Technical Review. Again, this is, hopefully, a pretty straightforward category. It comprises those papers which look around and see what technologies are available and in use today. Papers in this category range from "Review of Foreign Air Pollution Control Technology for BOF Fugitive Emissions" presented at the first symposium up to "An Air Pollution Control Equipment Inventory of the U.S. Steel Industry" which will be presented tomorrow. These reviews are also an important part of symposia on technology. The last thing we need is reinvention of the wheel or a failure to recognize that someone already has solutions to particular problems.

The third category I have selected is Quantification of Emissions and Effluents. I think this is an extremely important type of paper in that a knowledge of what pollution is emitted is extremely important in establishing regulatory programs and in establishing the needs for technology and the effectiveness of technology. I think the classification is clear enough; I do not need to point out examples. There have been a number in each of the three symposia.

My next category is Laboratory and Conceptual Studies. This is an important area because ideas have to start somewhere. There has to be some preliminary analysis to determine whether a process or technology has any potential for solving one of the environmental problems that have been defined. Clearly we need basic science and we need basic thinking. The types of papers that I have included here range from "Formation and Structure of Water Formed Scales" presented at the first symposium to the panel discussion at the current symposium on "Destruction of Hazardous Wastes in Iron and Steel Furnaces." As I say, these studies are quite important because it is clear that there is much room for new technology in the environmental control area. On the other hand, they generally represent technology which is a long way from utilization on an industrial scale, and a long way from providing the basis for realistic regulations applicable to the industry.

My next category is Pilot Studies. This is another pretty obvious title. It covers the next step from successful laboratory or conceptual work to trials on small scale to demonstrate the technical feasibility of the ideas. Again, the titles of the papers make these things obvious, so I will not cite any examples.

The next category is one that is dear to my heart: Demonstration. I believe that the most difficult part of the development of technology for environmental control in the steel industry is making things work. Because of the scale and difficult conditions encountered in the steel industry, no technology can be considered acceptable until it has been demonstrated and made to work on full-scale plant installations. I think that the major technical effort that has been expended by the steel industry over the years in environmental control has been in this area. Papers that would clearly be covered range from the "Coke Oven Door Seal Demonstration" in the first symposium to the paper, "Minimizing Recycled Water Blowdown from Blast Furnace Gas Cleaning Systems," being presented at this symposium. From the standpoint of disseminating knowledge on what can and cannot be done, and on how to do it and what it costs to do it, I think perhaps this is the most important category of papers that can be presented at a symposium such as this.

My next category is Environmental Assessments. An environmental assessment in my opinion is a study which looks at all environmental aspects of a process and, out of this, perhaps, develops an idea of what should and what should not be done in the way of regulation of specific environmental aspects of the process. There were a couple of papers at the first symposium clearly defined as environmental assessments. In last year's symposium, there was an "Environmental Appraisal of Reclamation Processes for Steel Industry Ironbearing Solid Wastes." I think the key factor of an environmental assessment is the multimedia approach; that it looks, not just to what are the emissions from a process, or what are its effluents, or what are its solid wastes, but it attempts to look at all media, all environmental effects, and in this way put the process in perspective.

My final category is one that I feel is extremely important today; that is, Cost/Effectiveness/Cost/Benefit Analyses. The terms, I think are self-defining. The importance of them I will talk of later. And the example I will present is one paper at the first symposium, "Coke Battery Environmental Control Cost Effectiveness."

Now that I have described my categorization of the various types of papers, I would like to look at how many papers fit into each of these categories. I would like to emphasize at this point that these categories are arbitrary, selected by me, and the assignment of papers to various categories involved a judgment in many cases. Nonetheless, I hope I have developed a reasonable breakdown of what has been presented.

Regulatory analyses started as a pretty significant part of the program, then dropped off, then increased again. Technical Reviews have remained at about the same level for the three years. Quantification of Emissions and Effluents started as a very significant part of the symposium, but has been dropping off ever since. I think that makes a great deal of sense. I think maybe it indicates that we have learned what the emissions and effluents from our processes are, so emphasis has turned from finding out what they are to doing something about them. Laboratory and Conceptual Studies started at a pretty low level, and then jumped to be a major part of the symposia. Perhaps this ties in with the previous item, that, now that we have got some problems well defined, it is time to come up with ideas for solving them. Pilot studies have remained relatively constant as a significant part of the symposium. Demonstrations have remained pretty much constant as a significant part of the symposium. The last two items, however, are different. Environmental assessments have dropped off. I think this represents a bad trend. I think it reflects thinking which has become compartmentalized. I think we are looking at too many problems in isolation. I think each regulator has been looking at narrow problems. And I think this narrow viewpoint is a mistake. Finally, Cost/Effectiveness/Cost/Benefit Analysis started at a very low level and has just disappeared from more recent symposia.

That pretty much concludes my analysis of where we have been of the who, what, where, to some extent the why of where we are today. Now I would like to look to the future within this same framework and project where I think we ought to go, and maybe give you an idea of what I think future symposia might best involve.

There are a number of things that we have to consider in projecting where we should go. One is the status of the nation's accomplishments at this point. We are now at the point where primary standards for air have been met in most areas, and are projected to be met in almost all areas within the next couple years. We are now at the point where essentially all of industry has installed Best Practicable Technology for water pollution control, and will have installed within a few years Best Available Technology for water pollution control. The recently issued report by Arthur D. Little for AISI, "Environmental Policy for the 1980's: Impact on the American Steel Industry," shows that the steel industry has installed equipment for control of 95% of its particulate emissions and will shortly have installed equipment for control of 96% of its emissions. Facilities installed or under construction will remove 91% of our water pollutants and within a few years will be removing better than 98% of our water pollutants. I think these factors must be considered in looking at future discussions of pollution control technology.

The Clean Air Act and Clean Water Act are both due to reauthorization and perhaps some fairly extensive revision in the near future. Changes in these laws, of whatever nature, will lead to regulatory changes and will lead to different requirements on the technology for the industry.

The ambient air standards, and specifically the standard for particulate matter, are under review right now and we can anticipate a major change in the near future. It appears that the controlled particulate will be changed from total suspended particulate to some finer particulate fraction. This type of change in standards will be accompanied by major upheaval in the type of regulations enforced, and possibly in the technology required to achieve the new standards.

We have in this country today a new administration dedicated to regulatory reform. Much of the regulatory reform will be directed at more cost/effective, cost/beneficial regulations. As these regulatory reforms are implemented, and I am sure they will be, it will be essential that we know more about the cost/effectiveness and cost/benefit of regulations on the books and of forthcoming regulations.

I have covered very quickly a whole series of factors which I think change the way we will be looking at iron and steel pollution abatement technology in the future. In light of all these factors, I would like to go back to a couple of my tables and say, here is what I think the emphasis should be in future symposia.

First of all, as to subject matter (Table 1): I anticipate there will be a change in the ambient air standard which will require changed emphasis in our approach to air pollution control for the industry. On water pollution control, I think we are approaching today the definition of Best Available Technology and when we have that defined, there will be less need and less interest in water pollution control technology developments. As the programs for solid waste control under RCRA become better defined, we will need to continue a significant emphasis on solid waste, but the big area of interest for the future I feel has to be on multimedia pollution control, on the impact of one type of pollution control on another, and on improving our overall environment, so I am looking for a major increase in multimedia papers.

As to types of papers (Table 3), I anticipate major changes in the regulatory patterns in this country for three reasons:

1. Because we are already approaching many of our goals.
2. Because I anticipate significant regulatory reform.
3. Because there will be changes in the Air and Water Acts.

Therefore, there will be a continuing need for further regulatory analyses.

I think there will be less need for technical reviews as time progresses. Progress is not so fast and changes are not so frequent that technical reviews are needed on a continuing basis. Quantification of emissions and effluents will change. We have developed a good idea of what our emissions and effluents are considering present standards and present knowledge. However, as the direction of regulatory control changes--for example, if we go to control of total thoracic particulate rather than total suspended particulates--we will need to know what are the emissions from the industry. So, there will be continuation but a change of emphasis in the area of quantification. As to laboratory and conceptual studies, I think we have, basically, the technology today to control pollution from the iron and steel industry. New ideas may come along and be developed, but we do not need the intensive search for methods we have had in the past. So, we may hear less of these in the future. There may be less on pilot studies for the same reason. Our problems will continue to be the application of technology.

Demonstration will continue to be the major issue. The application of technology will continue to be the principal technical problem of the industry and, therefore, I think the emphasis on demonstration must and should--and will--continue. As to my last categories, environmental assessments and cost/effectiveness/cost/benefit analyses, I think the time has come when these should be the major emphasis of our looking to the future. I think with a framework of air, water, and solid waste laws, we will be in a better position to assess the overall environmental impacts of any process change or any pollution control directed at one medium, and I think we will need more of this to achieve an adequate balancing of the overall needs of the environment.

As to cost/effectiveness/cost/benefit analyses, I think the time has come. In a time when the country is plagued with problems of energy, unemployment, inflation, and other new problems, we cannot continue to look on the environment as a goal set aside from all others. We must look at it in the perspective of social needs. The way to do this is by making sure when we do things that we are getting the biggest bang for the buck, and that the bucks we are spending are achieving something worthwhile. Now is the time to devote our intelligence and our energy to realistic cost/effectiveness/cost/benefit analyses in the environmental area.

One last point I would like to make is the question of who is to do the work in the future. We have talked about EPA, their contractors, steel companies, and others doing work, and we discussed the need for joint, cooperative work between EPA and the industry. I think there has been good cooperation in the past and I discussed this earlier. But I think there is one fault with what has been done in the past and one area where we must do better in the future. In the past, EPA has set up their programs and defined their objectives, and then sought assistance from AISI in carrying out these programs. We were very glad to give that assistance. But, back in school, in teaching us the scientific method, they always started with, first, define the problem. And I think that is one area where joint effort between industry and EPA can and should guide the programs of the future. I would like to see more joint input to research planning, in the analysis of what needs to be studied, and in the analysis of how to study those demnstrated needs. I think I can tell EPA that AISI stands ready to work with them to develop more effective programs to solve the technology problems of pollution control in the industry, not just from the Agency viewpoint, not just from the industry viewpoint, but, hopefully, from the nation's viewpoint.

THE UNFINISHED AGENDA: AN ENVIRONMENTALIST'S VIEW OF STEEL MILL AIR POLLUTION

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ABSTRACT

The steel industry has made substantial progress in controlling air pollution. Particularly noteworthy are efforts to control coke oven emissions in a comprehensive manner. In addition, several companies are developing non-capture systems to control fugitive emissions from iron and steelmaking facilities.

But the job is not done. Total suspended particulate levels still exceed the primary standards in major steelmaking areas of the country by a significant margin. Therefore, additional controls on process sources will be necessary. Attainment of the standards will also depend upon achieving good work practices. To make sure such practices become part of the daily operating routine, self-monitoring programs should be instituted at steel mills.

THE UNFINISHED AGENDA: AN ENVIRONMENTALIST'S VIEW OF STEEL MILL AIR POLLUTION

If you had picked up the newsletter of a local environmental group as recently as just 2 or 3 years ago, you would probably have found an article complaining about large visible clouds of smoke and fumes emanating from a nearby steel mill. The owners of the mill would have been severely criticized for failing to address these pollution problems in a timely manner.

Today that situation has changed to a certain extent. Though unresolved issues still exist, most notably the listing of coke oven emissions as a hazardous air pollutant, our group recognizes that the steel industry has made substantial progress in the overall control of particulate emissions. Further, we realize that the solutions have not always been simple because emission sources are numerous and quite varied.

But the job is not done. Total suspended particulate (TSP) levels still exceed the primary standards in major steelmaking areas of the country by a significant margin. To reach attainment, additional controls on process emission sources and the achievement of good work practices will be necessary.

Before I discuss these points,I would like to focus on control activities that have been taking place in the industry. Particularly noteworthy are efforts to control coke oven emissions in a comprehensive manner. One example is U.S. Steel's program for minimizing door leaks at Clairton Works where the company has upgraded existing door technology by using more temperature-resistant seals and plunger springs. In addition, guide/stop blocks have been added to each door to 1) prevent excessive stress on the sealing edge,and 2) produce better door sealing by repeatedly positioning the door in the same place. Finally, operating and maintenance (O&M) practices have been expanded at Clairton to provide more thorough inspection, cleaning and repair of doors.(1, 2)

Locally, a noticeable improvement in control performance has been made by Interlake at its two-battery coke plant. This accomplishment can be credited, in part, to a major overhaul of the facility. The larry cars have also been retrofitted with extra piping to help retain particulates in the coke plant's enclosed by-product systems. Finally, Interlake has installed a travelling hood/fixed scrubber system to reduce pushing emissions.

Recent developments indicate that more efficient pollution control technologies will be available to the industry in the near future. Several companies have been developing alternative approaches to control systems which first capture emissions and then transport them to air-cleaning devices. The incentive to explore such alternatives has been strong because of the costs associated with systems that totally enclose a building such as a blast furnace cast house and then evacuate it to a baghouse fabric fil

One development which has received a great deal of attention in the last few months is a non-capture system developed by Jones & Laughlin (J&L) to control cast house emissions. While little information about this system is available to the public because J&L has applied for a patent, I understand that it essentially reduces the amount of particulates produced in the first place by minimizing contact of hot slag and metal with the cast house atmosphere, thus suppressing the generation of iron oxide fumes. No capture hoods or air-cleaning devices are required.

U.S. Steel has also been investigating the feasibility of applying this concept at its mills. At Geneva Works, a recent test showed that cast house emissions could be suppressed to very low levels by using a flame to purge oxygen from the hot metal ladle before and during the cast. At South Works, U.S. Steel has devised a non-capture system at its electric arc shop consisting of a ring of steam jets attached to the top of the hot metal ladle. During the tap, steam is injected into the ladle to suppress the generation of fumes. This system has performed effectively.

These developments are very encouraging, particularly since they come at a time when some steel companies have shown a reluctance to further control fugitive process emissions. Instead, they have been focusing more attention on open dust sources. Though unpaved roads and raw material stock piles can be significant sources of air pollution, additional controls on process emission sources will also be necessary to achieve the primary standards.

At this point, I would like to briefly mention several studies which were commissioned by the U.S. Environmental Protection Agency for the purpose of supplementing local modeling efforts in heavily industrialized urban areas of the Midwest.

In one study, the role of open dust sources was investigated on days when the 24-hour primary standard for TSP was exceeded at a monitoring station located close to three steel mills in southeast Chicago. It was hypothesized that if violations of the 24-hour standard were primarily due to open dust, then few violations should occur on days when there was precipitation cover on the ground or when wind speeds were below critical thresholds (12 m.p.h.) for the entrainment of particulate matter from ground or from raw material storage piles.

During the two year study period, 228 days of TSP readings were made. Of these, 40 were greater than the 24-hour standard (260 micrograms per cubic meter). During these 40 days there was precipitation either greater than 0.01 inches on the sampling day or 0.1 inches the day before sampling on nine occasions. In other words, 22.5% of the 24-hour exceedences occured when the impact of open dust sources was minimal. Additionally, 29 days or 72.5% of the exceedences occured on days in which the resultant wind speed was less than 12 miles per hour.(3)

Microscopic analyses of particles found on high volume filters from monitoring sites near steel mills in northwest Indiana and Cleveland have also been informative. These analyses have identified, in general terms, the contributions of various source categories to TSP levels. Particles were identified by means of their morphology (structure and form), size, transparency, color and other physical properties. In addition, they were grouped into categories such as minerals, combustion products, biological matter and miscellaneous, with further subcatagorization where possible.

The concentrations on the filters frequently exceeded the primary and secondary 24-hour TSP standards. Analyses showed that no single source category was the sole cause of TSP standard excursion on any date or from date to date. For example, in one study open dust from raw materials handling activities contributed a large portion of the particle types on one sampling date, while on another date emissions from a steel melting process were indicated as the primary particle type.(4) In another study, emissions from iron melting as well as open dust from raw materials handling were found to be the major components of TSP at one monitoring site, while at a nearby site steel melting emissions were the primary component.(5)

These analyses are limited in capability. Both reference samples from the sources in question and meteorological data would be needed in most cases to accurately identify the particular operations in the steel mill which are responsible for the particles found on the filters. Nonetheless, they do point out the complexities of air quality problems in major steelmaking areas and the need for comprehensive control programs.

Even with a complete program directed at process and open dust sources, attainment of the primary standards for TSP will also depend upon the achievement of good work practices. This is obviously true in the case of controlling coke oven emissions where strict adherance to specific O&M practices is critcal, but the same can apply to other steel mill sources. For example, some companies have modified operating procedures at basic oxygen process shops to help reduce charging emissions. At J&L's Indiana Harbor Works, hot metal is poured into the vessel as slowly as possible to reduce agitation of the bath and splashing. In addition, the vessel is tilted as little as possible, thereby keeping its mouth close to the main collection hood in order to improve capture efficiency.

In some cases, manpower will be the key to achieving good O&M practices. Data on offtake leaks at Kaiser Steel's Fontana Works show that a substantial improvement in control of leaks occured after one additional employee was provided to help with luting topside leaks and tending the lids.(1)

To ensure that good work practices are established and that they become part of the daily operating routine, self-monitoring programs should be instituted at steel mills. Control performance at coke batteries, for example, could be determined by smoke readers recording visible emission observations. Steel companies in Pennsylvania have already instituted this practice in order to comply with state law.

One steelmaker has found self-monitoring programs to be very beneficial. According to CF&I, self-monitoring "helps to identify the cause rather than the symptom of a problem so that the trouble area or condition can be eliminated rather than just treated. It also monitors progress, obtains operator involvement, reinforces productive efforts, directs maintenance efforts, and documents improvements."(6)

An example of an instance in which self-monitoring could make a difference in control performance involves one of our local steel mills. Though several coke batteries at this mill have been modified for stage charging, visible emissions still range from 1000 to 1200 seconds per five consecutive charges. Even though a debate over what represents a "reasonable" level of control for charging emissions has been taking place, I believe there is room for considerable improvement at these batteries.

In addition to CF&I, I am aware of the self-monitoring program instituted by U.S. Steel - again at Clairton Works. The fact that both U.S. Steel and CF&I have achieved a great deal of success in controlling coke oven emissions illustrates the importance of self-monitoring for optimizing emission control. We hope more steelmakers will develop similar programs.

In conclusion, we recognize the special needs of the steel industry and we applaud the efforts which have been made to deal with them. However, violation of the primary standards still persist in major steelmaking areas. Additional time has been provided by the steel "stretch-out" bill to address pollution requirements and to modernize. Where strong efforts are being made to solve air quality problems by improving existing control systems and developing new technologies, the industry will receive our support.

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Session 1: AIR POLLUTION ABATEMENT

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INHALABLE PARTICULATE MATTER SAMPLING PROGRAM FOR IRON AND STEEL

AN OVERVIEW PROGRESS REPORT

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ABSTRACT

EPA's Office of Research and Development has entered into a major program to develop inhalable particulate (IP) matter emission factors, where IP is defined as airborne particles of <15 µm aerodynamic equivalent diameter. The Industrial Processes Branch of EPA's IERL-RTP is responsible for the ferrous metallurgical industry segment of this program. Efforts to date for the iron and steel category are summarized in this paper. IP requirements are meshed with those of other EPA sampling programs whenever possible, thus reducing overall cost to EPA and minimizing inconvenience to the host plants.

A thorough literature review and compilation of existing data revealed the existence of particle size data for several of the major iron and steel sources. However, none of these data were obtained using current IP measurement technology; most of them do not cover the full IP size range and, in many cases, there is insufficient documentation to completely determine test procedures followed and to fully define the process operation during the tests. The current field test program is designed to augment this existing data base by directing resources toward those sources with the combination of high priority and low existing data quality. Both process sources and open sources are included. To date, processes tested are basic oxygen furnace (BOF) charging and tapping, hot metal desulfurization, blast furnace cast house (both building evacuation and local control technologies), sinter discharge, and BOF main stack (limited combustion system after scrubber). Open sources tested are paved and unpaved roads and coal storage pile maintenance, all both with and without controls, and an uncontrolled open area. Several additional tests are underway or scheduled. All data gathered will be summarized and published in a single report early next year.

INTRODUCTION

The U.S. Environmental Protection Agency is required, under the amended Clean Air Act of 1977, to review the scientific basis for the total suspended particulate ambient air quality standard. Major consideration is being given to a size-specific particulate standard. EPA has initiated an extensive program to compile and review existing data and, where necessary, conduct field sampling programs from which reliable size-specific emission factors can then be determined.

EPA's Office of Research and Development is responsible for developing these inhalable particulate emission factors. A major part of this effort is directed toward the steel industry. In this paper, the rationale and approach being followed to select test sites are discussed. This paper also discusses briefly the review of existing iron and steel source particle size data, the field sampling program being undertaken, and results obtained to date.

DISCUSSION

Source Selection

At the commencement of the size-specific emission factors development program, the aerodynamic equivalent particle diameter upper cut point was set at 15 μm. This was defined as inhalable particulate (IP)(1). The Clean Air Science Advisory Committee recently reviewed the basis for a size-specific standard; based on this review, the upper cut point diameter may be reduced to 10 μm. This change will not affect the field sampling protocols(2-5) which require, for example, the use of cascade impactors with a 15 μm precutter cyclone for ducted emissions. The precutter is still required to remove large particles which, if allowed to enter the impactor, would tend to bounce from one stage to another, thus giving erroneous stage weights. Lowering the upper cut point would expand the data base since most of the existing data were gathered with devices having an upper cut point of about 10 μm.

At the outset of the iron and steel IP sampling program, the decision was made to proceed with field test site selection on a voluntary source basis, rather than through the application of Clean Air Act, Art. 114. Industry was contacted through the American Iron and Steel Institute (AISI) which established an ad hoc coordinating committee. Meetings with this committee were held to present an overview of the whole program and, following resolution of outstanding issues, to review sources selected for testing.

The EPA/AISI cooperative effort has thus far resulted in several field test programs. Armco, Inc.'s Middletown Works was selected for measurment of open source emissions and their BOF stack. Inland Steel Co.'s sinter discharge and Armco, Inc.'s Kansas City electric furnace shop will be tested during October. J&L Steel's full combustion BOF stack at Aliquippa will be tested in November as will U.S. Steel's Fairfield Q/BOP.

In addition to the selection procedure coordinated with AISI, every effort has been made to combine measurement of IP with other EPA sampling programs. Not only does this reduce EPA expenditures, it also reduces inconvenience to the host companies. In this category, tests have been completed at Kaiser Steel Co.'s new BOF shop (charging and tapping fugitives) and hot metal desulfurization. Dominion Foundries and Steel Co. was the site of a blast furnace cast house test; measurements at their No. 1 coke quench tower are now in progress. Finally, Bethlehem Steel Co.'s "L" blast furnace cast house at Sparrows Point was tested in April.

The initial source priority ranking, shown in Table 1, was developed based on estimated controlled total particulate emissions from each source on a nationwide basis. This prioritization represented an average of emission factors developed under separate efforts: one represented factors from specific short term emission tests (6); the other, presented values which might be termed typical for long term operation (7). Although this procedure was only qualitative, it did nevertheless provide a rational approach for initial source selection.

Review of Existing Data

The initial source selection priority list was based on total particulate data due to the paucity of known particle size data. At the outset of this program 2 years ago, only six particle size data sets from iron and steel sources were contained in EPA's Fine Particle Emissions Information System (FPEIS)(8). These data sets, consisting of three open hearth furnace stack tests, two electric arc furnace tests, and a coke oven pushing shed test, are summarized in Figures 1-3, respectively. These data are judged to be good, although consideration must be given to when they were obtained (1974-77) and the advancements made in particle size sampling technology since then. Ideally, these three sources should be tested again but not before other high priority sources with no existing data are tested.

A thorough review of both published and unpublished literature was recently completed by GCA/Technology Division in a concerted effort to ferret out all existing particle size data(11). This review produced over 30 unpublished test reports containing particle size data. None of these data were obtained using the current IP measurement technology. It is apparent, however, that many of these data are of sufficient quality to warrant delaying new tests of these sources until high priority sources with little or no data are tested.

The initial source test priority has been revised to reflect the discovery of these size-specific data. Table 1 also indicates the revised rank of each source and also the amount and type of data gathered. In

TABLE 1. IRON AND STEEL SOURCE TEST PRIORITY RANKING (CONTROLLED EMISSIONS)

Rank					
Initial	Revised	Process	Industry Total Particulate Emissions, Mg/yr[(a)]	Data Sets Discovered[(b)]	IP Test Planned
1	1	Coke Quenching	34,500	2(b), 2(d)	X
2	2	Blast Furnace Cast House	22,700	1(d)	X
3	3	BOF Stack	20,000	-	X
4	4	Material Stockpiles	16,300	6(f)	X
5	5	Roadway Travel	16,300	7(f)	X
6	27	Coke Combustion Stack	16,300	3(b), 4(d), 1(e)	
7	6	BOF Charge and Tap	14,500	2(b), 2(c)	X
8	28	Coke Pushing	8,900	5(b), 1(d), 1(e)	
9	29	Sinter, Misc. Fugitives	8,700	2(d)	
10	30	Sinter Windbox	8,200	7(b), 1(d), 1(e)	
11	7	EAF Charge, Tap, Slag	7,600	-	X
12	14	Coal Preparation	7,400	-	
13	31	OH Stack	7,300	1(b), 3(d)	
14	10	Coke Door Leaks	7,100	-	
15	8	EAF Stack	6,600	1(b), 1(d)	X
16	9	Sinter Discharge End	5,700	1(b)	X
17	11	Blast Furnace Top	3,700	-	
18	12	Teeming	3,700	-	
19	13	Ore Screening	3,300	-	
20	15	BOF Misc. Fugitives	2,200	-	
21	16	Coke Topside Leaks	2,100	-	
22	17	Reheat Furnaces	2,000	-	
23	18	Blast Furnace Combustion	2,000	-	
24	19	OH Roof Monitor	2,000	-	
25	32	Coal Charging	1,800	2(d)	
26	20	Open Area	1,100	-	
27	21	Machine Scarfing	670	-	
28	22	BOF HMT	650	-	
29	23	OH Misc. Fugitives	640	-	
30	24	Soaking Pits	570	-	
31	25	EAF Misc. Fugitives	540	-	
32	26	OH - HMT	190	-	

(a) Megagrams per year (= Metric tons per year).

(b) Particle Sizing Method: a - follows IP protocol, b - impactors, good process data taken; c - SASS train; d - Coulter counter, sieve, or microscopic; e - test methods unknown; f - exposure profile/wind tunnel with impactor.

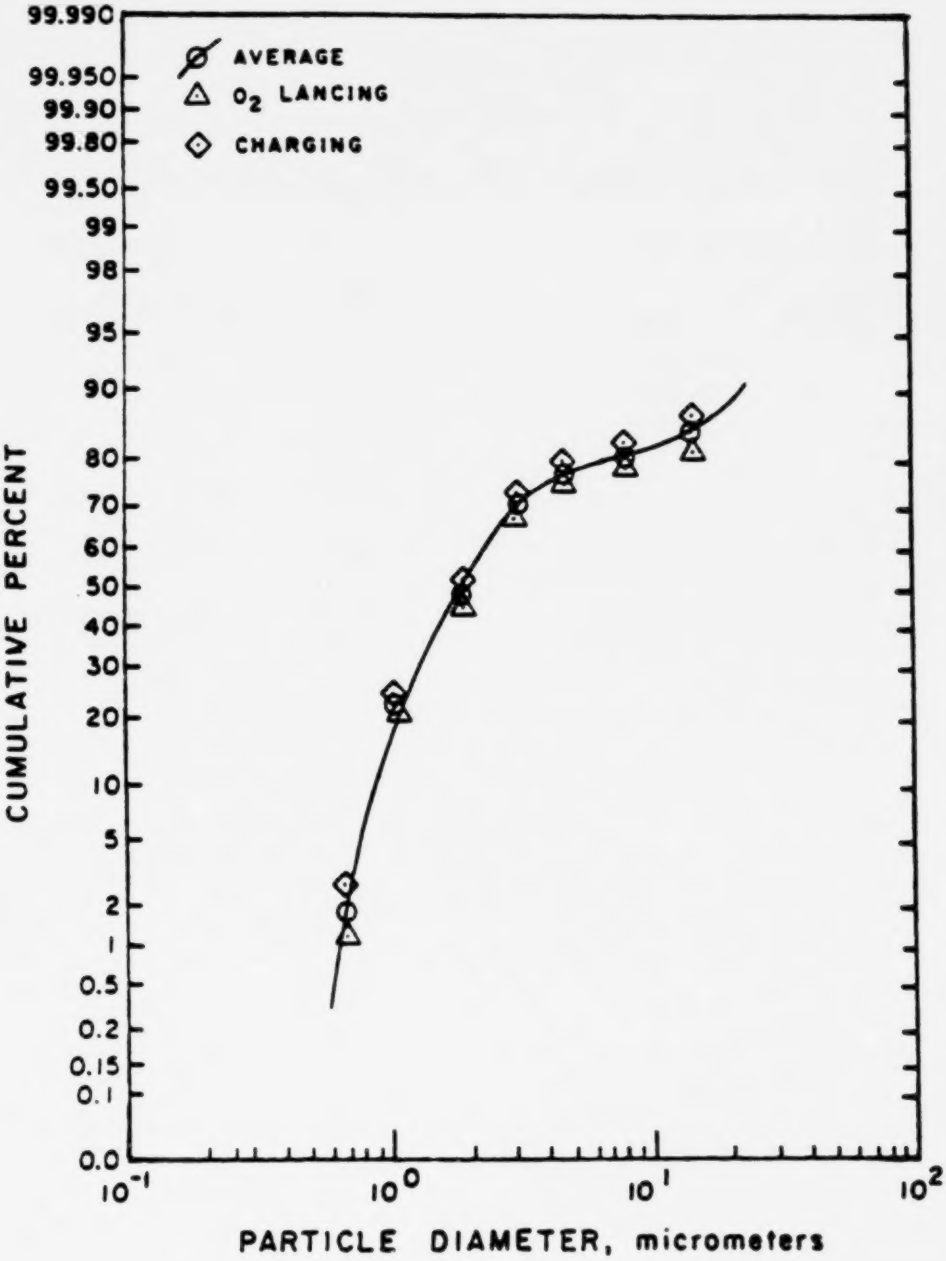

Figure 1.(9) Average size distribution - open hearth furnace emissions, uncontrolled.

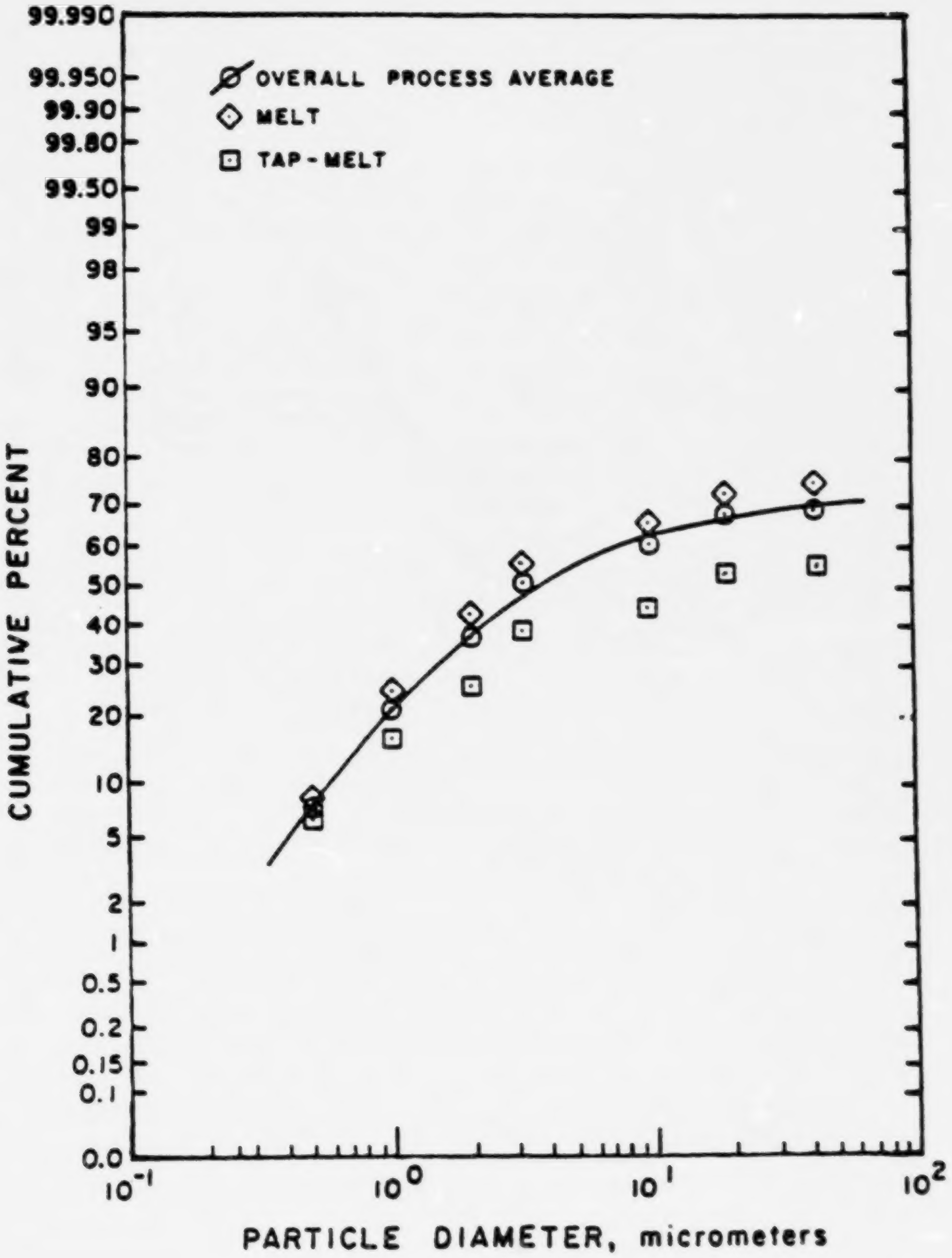

Figure 2.(9) Average size distribution - Marathon LeTourneau electric arc facility.

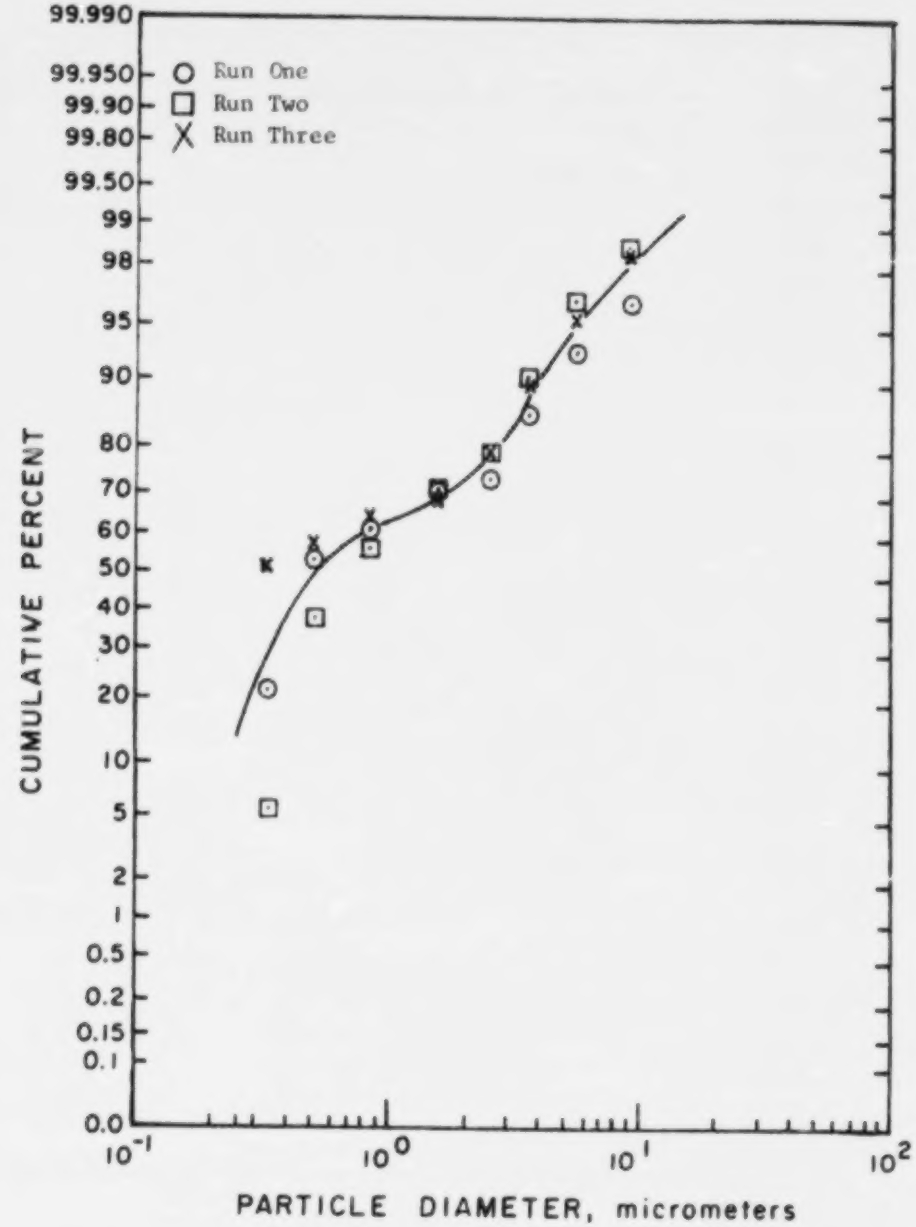

Figure 3.[10] Average particle size distribution--coke oven pushing.

addition those sources which have been or will be tested under this IP program are also shown in Table 1.

Results to Date

The following briefly summarizes the test results available to date.

Armco Inc., Middletown Works

The extensive source fugitive emissions program undertaken for EPA by Midwest Research Institute at Armco, Inc.'s Middletown Works will be addressed in detail by the next speaker(12). Later this afternoon, Bruce Steiner will address the specific control strategies instituted under Armco's bubble application(13).

In summary, emissions from paved and unpaved roads were measured before and after the initiation of emission reduction procedures. For paved roads, this procedure consisted of water flushing and/or sweeping-vacuuming at regular intervals. Berms were treated with Coherex®. Unpaved roads were treated either with Coherex® or water, also at regular intervals. Tests of the Coherex® treated road were conducted on the second and third days after suppressant application. Additional tests would be required to determine the long term control efficiency decay. Windblown emissions from a coal pile during pile maintenance operations were also measured. The Armco/Middletown open source tests are summarized in Table 2.

The Middletown limited combustion BOF main stack was tested for IP in July 1980(15). Although the IP protocol calls for measurements before and after the control device, the nature of the limited combustion BOF operation at Middletown precluded measurements before the scrubber. Measurements after the scrubber included total particulate and particle size as per the protocol. The results, shown in Table 3, are presented for two production rates, normal and intermediate. The ratios of IP to total particulate are 69 and 57 percent, respectively, for the controlled emission.

Kaiser Steel Corporation

The first two sources tested under the iron and steel IP program were the hot metal desulfurization (HMDS) and BOF charging and tapping emission control systems recently installed at Kaiser Steel Corporation's Fontana, CA, plant. These tests, performed in coordination with and cost-shared by EPA's Office of Enforcement through EPA's Region V office, consisted of total particulate by EPA Method 5 and particle size before and after the control device (in both cases, a baghouse). EPA's contractor, Acurex Corporation, conducted this extensive source test program during March-May 1980.

Results of the HMDS tests reported at last year's EPA Iron and Steel Symposium(16) have been revised due to recent improvements in the data reduction procedure. The revisions resulted in a lowering of the total particulate emision factors accompanied by an increase in the IP fraction.

TABLE 2. SUMMARY OF ARMCO, INC., MIDDLETOWN OPEN SOURCE FUGITIVE EMISSION MEASUREMENTS (14)

Source	Vehicle Type	Control Measure	Particulate Emission Factor g/VKT[a]		
			Total	<15 μm	<2.5 μm
Paved Roads					
Overall Ave.	Mix	Uncontrolled	599	158	40
Test Site A	Mix	Uncontrolled	478	114	30
Test Site A	Mix	Vacuum Sweeping	164	92	25
Test Site D	Mix	Uncontrolled	1070	298	69
Test Site D	Mix	Flushing	680	336	96
Unpaved Roads					
Test Site B	Light Duty	Uncontrolled	3320	864	269
Test Site B	Light Duty	Coherex®	252	57	20
Test Site C	Heavy Duty	Coherex®	1530	321	43
Test Site E	Heavy Duty	Uncontrolled	34075	4382	1070
Test Site E	Heavy Duty	Water[b]	2400	237	59
Test Site E	Heavy Duty	Water[c]	8300	3410	610
Coal Storage Pile Maintenance	Dozer	Uncontrolled	845[d]	505[d]	405[d]

(a) Grams per vehicle kilometer traveled unless otherwise indicated.

(b) Immediately after application.

(c) 75 min. after application.

(d) Grams per minute of dozer activity.

TABLE 3. SUMMARY OF LIMITED COMBUSTION BOF MAIN STACK PARTICULATE EMISSION FACTORS(15)

Date	Run Nos.	Cumulative Emission Factor, kg/Mg (lb/ton) Steel(a)				Low Carbon Steel Produced, Mg (tons)
		<2.5 μm	<10 μm	<15 μm	Total	
7/11/80 through 7/14/80	PSD-1 (b)- PSD-6	0.010 (0.020)	0.010 (0.021)	0.011 (0.022)	0.016 (0.031)	196 (216)
7/14/80	PSD-7 (c) and PSD-8	0.007 (0.013)	0.007 (0.014)	0.008 (0.015)	0.014 (0.027)	152 (168)

(a) Steel produced.

(b) Results are the average of the first three heats and are considered to represent emissions during normal production rates.

(c) Results are for the last heat tested and represent emissions for intermediate production rates.

The revised emission factor for the uncontrolled fume generated is 0.54 kg/Mg of hot metal desulfurized (range: 0.23 to 0.77 kg/Mg). The average IP fraction was 32.2 percent. The revised baghouse outlet emission factor is 0.0015 kg/Mg of hot metal desulfurized (range: 0.0011 to 0.0017 kg/Mg). The revised average IP fraction was 81.1 percent. Baghouse collection efficiency averaged 99.7 and 99.3 percent for total and IP particulate, respectively.

Separate measurements of hot metal charging and tapping emissions were made on the No. 6 BOF. These emissions are collected by hoods in the furnace enclosure (doghouse) and conveyed to the baghouse. Uncontrolled emissions were measured simultaneously in the two main fugitive emission ducts serving No. 6. This site was chosen for its accessibility and noninterference from other emission sources ducted to the baghouse. Controlled emissions were measured in 2 of the 12 baghouse exit stacks only during periods when No. 6 was charging or tapping and other sources ducted to the baghouse were not generating emissions.

Dominion Foundries and Steel Company (DOFASCo)

DOFASCo first installed cast house emissions control several years ago. The combined control system for cast houses No. 2 and 3 was started up in November 1978. These cast houses are evacuated by a common fan and baghouse sized to control emissions in either one by isolation valves.

The IP emission tests were run during the week of November 10, 1980, on the combined control system serving cast houses No. 2 and 3; however, measurements were made only when furnace No. 3 was casting. Emission tests followed the protocol for ducted sources. Measurements of the fume generated were made for EPA/IERL-RTP and EPA's Office of Enforcement through EPA's Region III office by GCA/Technology Division in the duct upstream of the baghouse. A detailed discussion of the preliminary results was presented at the Third Symposium on the Transfer and Utilization of Particulate Control Technology(17). Uncontrolled total particulate emissions averaged 0.2 kg/Mg iron cast. Average IP fraction was reported as 62 percent; revisions and corrections to the IP data reduction scheme currently being implemented may change this value. In this case, only the IP fraction value will be affected by these revisions.

Bethlehem Steel Corporation, Sparrows Point

GCA/Technology Division conducted emission tests for EPA/IERL-RTP and EPA's Office of Enforcement through EPA's Region III office at the new "L" furnace cast house at Sparrows Point during April. This is a large modern furnace employing close-fitting hoods and covers over the trough, iron runners, and spouts, a practice pioneered in Japan. These and other fugitive emissions are ducted to a large baghouse. Emissions, following the ducted source protocol, were measured in the duct upstream of the baghouse. Since this baghouse also controls emissions from many other fugitive sources, the discharge emissions would not be representative of casting emissions. Therefore, the open monitor discharge was not sampled.

Preliminary data analysis indicates an average total uncontrolled particulate emission factor of 0.65 kg/Mg hot metal cast. The particle size distribution is being recalculated in light of revisions to the data reduction program. Initial indications are that the IP fraction is somewhat less than was measured at DOFASCo. These results, compared to the DOFASCo results, seem reasonable since local evacuation should also capture the large particles which would have settled out in the DOFASCo cast house and would, therefore, not have been captured by the roof monitor exhaust.

Future Tests

Five additional IP field sampling tests are either underway or scheduled. The No. 1 quench tower at DOFASCo is now being tested; field work will be completed by the end of October. This is a complex project with partial funding by EPA/IERL-RTP, EPA's Office of Air Quality Planning and Standards, EPA's Division of Stationary Source Enforcement, and DOFASCo. Emission measurements are being made above and below the baffles. Separate tests will be run at two quench water qualities: one using coke plant wastewater as makeup to the sump; and the other, Lake Erie water. Three particle sizing techniques are being used: Andersen Mark III with a 15 μm precutter cyclone, Southern Research Institute's two-cyclone IP train, and the EPA/Southern Research Institute dilution train.

Inland Steel Co.'s sinter plant discharge emissions will be sampled in October. Measurements will be taken before and after the baghouse.

The J&L Aliquippa BOF main stack ESP is scheduled for tests in November. IP measurements will be made before and after the ESP. This will be a jointly funded test involving EPA/IERL-RTP, EPA's Office of Air Quality Planning and Standards, and EPA's Office of Enforcement through EPA's Region III office.

U.S. Steel's Fairfield Q/BOP main stack is also scheduled for tests in November. IP measurements will only be made after the scrubber due to the difficulty of installing ports prior to the quencher.

Armco, Inc's. Kansas City electric furnace shop will be tested separately for main furnace emissions and for fugitive emissions captured by the canopy hood. Measurements, to be made before and after the control devices, are tentatively scheduled for November.

Once the above field tests are completed and each test report reviewed by EPA and the host plant, all data, new and old, will be summarized and published in one source category document giving emission factors versus particle size for all sources in the iron and steel industry for which data are available. In addition to the source test data, emission factors will be summarized in formats appropriate for AP-42(18). It is anticipated that testing will be completed in November and the iron and steel category report published in March 1982. These data will then be available to the states for the preparation of revised state implementation plans if a size-specific ambient air particulate standard is adopted.

ACKNOWLEDGEMENTS

The three sampling contractors for EPA's IP program are GCA/Technology Division, Midwest Research Institute, and Acurex Corporation. The AISI and its member companies (in particular Armco, Inc., Bethlehem Steel Corporation, Dominion Foundries and Steel, Ltd., Kaiser Steel Corporation, J&L Steel Co., and U.S. Steel Corporation) have been most helpful. EPA's Office of Enforcement and EPA's Office of Air Quality Planning and Standards were instrumental in developing and implementing the jointly funded tests. The cooperation of Environment Canada and the Ontario Ministry of Environment is also appreciated.

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COST EFFECTIVENESS EVALUATION OF ROAD DUST CONTROLS

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ABSTRACT

Preliminary analysis of control measures for fugitive particulate emission sources in the iron and steel industry indicates that control of open dust sources has a highly favorable cost effectiveness ratio in comparison with control of process sources of fugitive particulate emissions. However, rigorous cost effectiveness evaluation must await accurate and well documented information on control performance and cost. This paper addresses the analytical and practical considerations involved in acquiring meaningful cost effectiveness data for the major open dust sources in the iron and steel industry--vehicular traffic on unpaved and paved roads.

Results of extensive performance testing of road dust controls are presented. The control measures tested were watering and chemical treatment of unpaved roads and vacuuming, flushing, and broom sweeping of paved roads. The mean efficiencies of control measures tested, except for vacuum sweeping of paved roads, were found to be independent of particle size. The mean control efficiency of freshly applied Coherex® to unpaved roads was higher than the efficiencies of the other measures tested. An analytical framework for control cost effectiveness analysis is proposed, and control cost data for road dust controls at two steel plants are given.

INTRODUCTION

Previous studies of fugitive particulate emissions from integrated iron and steel plants have provided strong evidence that open dust sources (specifically vehicular traffic on unpaved and paved roads and storage pile activities) should occupy a prime position in control strategy development.[1,2] These conclusions were based on comparability between industry-wide uncontrolled emissions from open dust sources and typically controlled fugitive

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emissions from major process sources such as steel-making furnaces and sinter machines. Moreover, preliminary cost-effectiveness analysis of promising control options for open dust sources indicated that control of open dust sources might result in significantly improved air quality at a lower cost in relation to control of process sources. These preliminary conclusions warranted the gathering of more definitive data on control performance and costs for open dust sources in the steel industry.

As a result, a field sampling program was undertaken to obtain data on the performance of control measures for vehicular traffic on unpaved and paved roads within integrated iron and steel plants. A 1978 emissions inventory of open dust sources within the steel industry had shown that vehicular traffic accounts for approximately 70% of suspended particulate emissions on an uncontrolled basis.[2] The selection of control measures to be tested was based on the extent of use within the industry and the results of the preliminary evaluation of cost effectiveness of control options for unpaved and paved roads. Control measures selected for unpaved roads were watering and chemical treatment; and control measures selected for paved roads were vacuum sweeping, flushing, and a combination of broom sweeping and flushing.

The study design was developed to provide the following data needs for cost-effectiveness evaluation of each control measure tested:

1. Emission factors for three particle size fractions: total particulate (TP); inhalable particulate (IP)--particles smaller than 15 μm equivalent aerodynamic diameter (EAD); and fine particulate (FP)--particles smaller than 2.5 μm EAD, before and after application of the control measure.

2. Emission factor correction parameters for uncontrolled and controlled test road segments, providing adequate characterization of road surface and traffic conditions.

3. Control application parameters: intensity, frequency, and time after application.

4. Investment and operating costs of control.

TEST METHODS

Table 1 lists the equipment that was used to sample particulate emissions from traffic on unpaved roads and paved roads. Equipment locations and intake heights are specified. The primary tool for quantification of emission rate was the exposure profiler, operated in the moving point source mode.

The exposure profiler consisted of a portable tower supporting an array of five sampling heads. Each sampling head was operated as an isokinetic exposure sampler directing passage of the flow stream through a settling chamber (trapping particles larger than about 50 μm in diameter) and then upward through a standard 8 by 10 in. glass fiber filter positioned horizontally. Sampling intakes were pointed into the wind, and sampling velocity of each intake was adjusted to match the local mean wind speed, as determined prior to each test. Throughout each test, wind speed was monitored by recording anemometers at two heights, and the vertical profile of wind speed was determined by assuming a logarithmic distribution. Normally, the exposure profiler was positioned at a distance of 5 m from the downwind edge of the road.

TABLE 1. SAMPLING EQUIPMENT FOR EXPOSURE PROFILING

Distance from source (m)	Equipment	Intake height (m)
Upwind 10	1 Standard Hi-Vol	2.0
	2 Hi-Vols with 15 μm Inlets	1.0 3.0
	1 Continuous Wind Monitor	4.0
Downwind 5	1 MRI Exposure Profiler with 5 Sampling Heads	1.0 2.0 3.0 4.0 5.0
	2 Hi-Vol Parallel-Slot Cascade Impactors with Cyclone Precollectors	1.0 3.0
	2 Warm-Wire Anemometers	1.0 3.0

Particle size distribution in the dust emission plume was measured using a high-volume parallel-slot cascade impactor preceded by a cyclone preseparator. This provided for direct isokinetic measurement of the total particle size distribution but required extrapolation from the cyclone cutpoint (11 μm EAD) to determine IP concentrations. Particle sizing samplers were operated along side of the exposure profiler at two heights.

Also, a high-volume sampler (Hi-Vol) with a size-selective inlet (SSI) was operated at the upwind monitoring station to determine the IP fraction of the background particulate. For tests of controlled emissions, a second Hi-Vol/SSI was operated at a higher elevation to determine the change of background IP concentration with height. Conventional high-volume samplers were operated at one height both upwind and downwind of the source.

In addition to the measurements of wind speed obtained at two heights on the profiling tower, a meteorological instrument was also located at the background monitoring station. Continuous measurements of wind speed and direction at a height of 4 m were recorded at the upwind site.

In order to determine the properties of aggregate materials being disturbed by the action of machinery or wind, representative samples of the materials were obtained for analysis in the laboratory. Unpaved and paved roads were sampled by vacuuming and broom sweeping to remove loose material from lateral strips of road surface extending across the traveled portion.

Throughout a test of traffic generated emissions, a vehicle count was maintained by a pneumatic-tube traffic counter. Periodically (e.g., during 15 min of each hour) vehicle mix was determined by compiling a log of vehicles passing the test point segregated by vehicle type (number of axles and wheels). Vehicle speeds were measured with a radar gun. Data on vehicle weight were obtained from plant personnel.

At the end of each run, the collected samples of dust emissions were carefully transferred to protective containers within the MRI instrument van. Glass fiber filter from the MRI exposure profiler and from standard Hi-Vol units and impaction substrates were folded and placed in individual envelopes. Dust that collected on the interior surfaces of each exposure probe was rinsed with distilled water into separate glass jars. Dust was transferred from the cyclone precollectors in a similar manner.

Dust samples from the field tests were returned to MRI and analyzed gravimetrically in the laboratory. Glass fiber filters and impaction substrates were conditioned at constant temperature and relative humidity for 24 hr prior to weighing, the same conditioning procedure used before taring. Water washes from the exposure profiler intakes and the cyclone precollectors were filtered after which the tared filters were dried, conditioned at constant humidity, and reweighed.

After the gross samples of surface particulate were taken to the laboratory, they were prepared for moisture and silt analysis. The first step consisted of reducing the sample to a workable size. A riffle sample splitter was used for this purpose, following the principles of ASTM Method D2013-72, as appropriate.

The reduced samples of surface particulate were dried to determine moisture content and screened to determine the weight fraction passing a 200 mesh screen, which gives the silt content. A conventional shaker was used for this purpose. The procedures for moisture and silt analysis were patterned after ASTM Method C136-76.

TEST DESCRIPTION AND RESULTS

The field sampling of emissions, with and without control application, was performed at Armco's integrated iron and steel plants in Middletown, Ohio and Houston, Texas. At the Middletown works, testing was conducted in

July 1980 and in October and November 1980; in August 1980, Armco implemented an extensive control program for open dust sources at that plant. The control measures tested at the Middletown works included treatment of unpaved roads with Coherex® and with water and vacuuming of paved roads. At the Houston works, testing was conducted in June and July of 1981. The control measures tested in Houston were flushing of paved roads and a combination of flushing and broom sweeping of paved roads.

Testing of uncontrolled emissions was conducted either at sites where no control measures had been used or where control measures had been suspended allowing the source to return to its uncontrolled state. Whenever possible, a control measure was introduced and tested at the same location where the uncontrolled tests had been performed.

Emission factors and control efficiencies were obtained for TP, IP, and FP matter, as shown in Tables 2, 3, and 4, respectively. It should be noted that the mean efficiencies of the control measures tested, except for vacuuming of paved roads, were nearly independent of particle size.

Much of the observed variation in the controlled emission factors reflects differences in time between the control application and emissions testing. Except for the treatment of unpaved roads with Coherex®, the mean control efficiencies presented are thought to represent average controlled conditions. The control efficiencies for the application of Coherex® to unpaved roads reflect only the early stage in the lifetime of that control measure.

In the case of Coherex® application to unpaved roads traveled by light-duty vehicles, a well-defined initial decay in efficiency was observed for TP, IP, and FP (Figure 1). This is thought to reflect the effect of buildup of surface dust loading on the treated road because of vehicular tracking of material from adjacent unpaved areas. The curve for TSP in Figure 1, which was obtained in a previous study,[2] reflected the accentuated tracking effects resulting from the short length of the test strip.

CONTROL COSTS

Cost data for the control measures tested were obtained from the steel plants where testing was performed. These data included: (a) annualized costs of equipment purchase and installation, and (b) annual operating costs. The annualized investment costs took into account the initial costs, the lifetime of the equipment, interest, and taxes. To calculate the total annualized cost, the average annual cost of operation was added to the product of the initial capital investment and the capital recovery factor. The capital recovery factor is the percentage of the initial investment which would be paid yearly on a loan of mortgage. Table 5 presents a summary of the cost data obtained.

TABLE 2. TEST RESULTS SUMMARY FOR TOTAL PARTICULATE EMISSIONS

Test type	Control measure	Number of tests	Emission factor (lb/VMT)		Control efficiency (%)
			Range	Mean ± standard deviation	
Paved Road	Uncontrolled				
	Middletown	7	0.29-4.6	2.3 ± 1.5	-
	Houston	4	2.9-3.7	3.1 ± 0.41	-
	Vacuum sweeping	4	0.24-1.2	0.69 ± 0.38	70, 65*
	Flushing	3	1.0-1.6	1.2 ± 0.29	61, 58*
	Flushing and broom sweeping	4	0.51-1.8	1.0 ± 0.55	67
Unpaved road (light-duty traffic)	Uncontrolled	4	10-14	12 ± 1.9	-
	Coherex®	5	0.089-1.3	0.88 ± 0.50	92
Unpaved road (heavy-duty traffic)	Uncontrolled	4	99-130	120 ± 16	-
	Coherex®	4	3.4-8.5	5.4 ± 2.2	96
	Watering	2	8.3-29	19 ± 15	50**

* Based only on uncontrolled testing at the same site.

** Based on an 8 hr watering cycle.

TABLE 3. TEST RESULTS SUMMARY FOR INHALABLE PARTICULATE EMISSIONS

Test type	Control measure	Number of tests	Emission factor (lb/VMT)		Control efficiency (%)
			Range	Mean ± standard deviation	
Paved Road	Uncontrolled				
	Middletown	7	0.14-1.4	0.66 ± 0.42	-
	Houston	4	0.55-1.2	0.95 ± 0.28	-
	Vacuum sweeping	4	0.15-0.69	0.37 ± 0.24	44, 47*
	Flushing	3	0.27-0.58	0.41 ± 0.15	56, 62*
	Flushing and broom sweeping	4	0.095-0.44	0.23 ± 0.15	76
Unpaved road (light-duty traffic)	Uncontrolled	4	1.0-4.2	3.0 ± 1.4	-
	Coherex®	5	0.061-0.38	0.27 ± 0.14	91
Unpaved road (heavy-duty traffic)	Uncontrolled	4	26-34	30 ± 4.2	-
	Coherex®	4	1.2-2.0	1.5 ± 0.37	95
	Watering	2	0.99-4.7	2.8 ± 2.6	63**

* Based only on uncontrolled testing at the same site.
** Based on an 8 hr watering cycle.

TABLE 4. TEST RESULTS SUMMARY FOR FINE PARTICULATE EMISSIONS

Test type	Control measure	Number of tests	Emission factor (lb/VMT) Range	Emission factor (lb/VMT) Mean ± standard deviation	Control efficiency (%)
Paved Road	Uncontrolled				
	Middletown	7	0.050-0.33	0.18 ± 0.091	-
	Houston	4	0.15-0.43	0.28 ± 0.13	-
	Vacuum Sweeping	4	0.039-0.20	0.12 ± 0.077	36, 35*
	Flushing	3	0.060-0.076	0.068 ± 0.0079	75, 65*
	Flushing and broom sweeping	4	0.0042-0.11	0.074 ± 0.026	73
Unpaved road (light-duty traffic)	Uncontrolled	4	0.24-1.3	0.86 ± 0.44	-
	Coherex®	5	0.032-0.094	0.067 ± 0.023	92
Unpaved road (heavy-duty traffic)	Uncontrolled	4	5.5-8.8	7.6 ± 1.5	-
	Coherex®	4	0.27-0.59	0.46 ± 0.14	94
	Watering	2	0.22-1.0	0.62 ± 0.57	67**

* Based only on uncontrolled testing at the same site.
** Based on an 8 hr watering cycle.

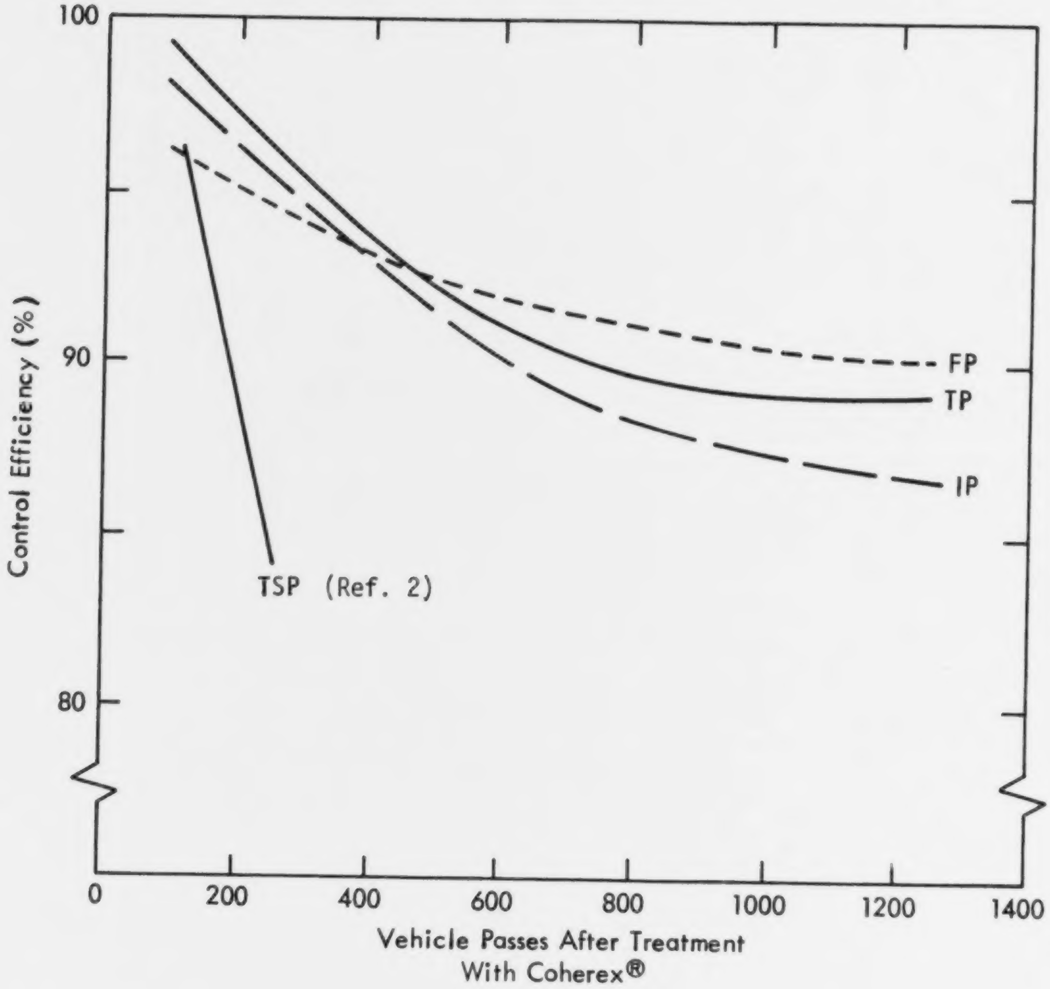

Figure 1. Initial Decay Curve for Control Efficiency of Coherex® Applied to Unpaved Roads.

TABLE 5. SUMMARY OF OPEN DUST CONTROL COST DATA

Plant	Source	Actual source extent (miles)	Control	Purchase and installation cost ($)	Year of purchase	Estimated lifetime (yr)	1980 operating and maintenance costs ($)	1980 treated source extent (miles)
Middletown works	Paved roads	16.9	2 Vacuum sweepers	144,000	1980	5	214,000	2,020
			Flusher	68,000	1976	10	57,000	5,080
	Unpaved roads	7.1	Coherex®, distribution truck, and storage tanks	100,000	1980	7	287,000	1,630
Houston works	Paved roads	14.6	Broom sweeper No. 1	18,000	1978	5	65,100	888
			Broom sweeper No. 2	20,000	1980	5	57,000	888
			Flusher	34,000	1978	7	52,300	1,776

Care must be taken in compiling figures for the items presented in Table 5 so that all of the costs are properly accounted for. Purchase and installation costs must include cost for freight, tax, and loan interest. The lifetime of the control application equipment is difficult to estimate because of lack of experience in using this equipment. The operating and maintenance costs should reflect increasing frequency of repair as the equipment ages, along with increasing costs for parts, energy, and labor. The treated source extent, which is the product of the mileage of roads treated and the annual number of treatments, requires accurate recordkeeping on the use of control application equipment. Figure 2 depicts the variations in costs over the lifetime of the application equipment.

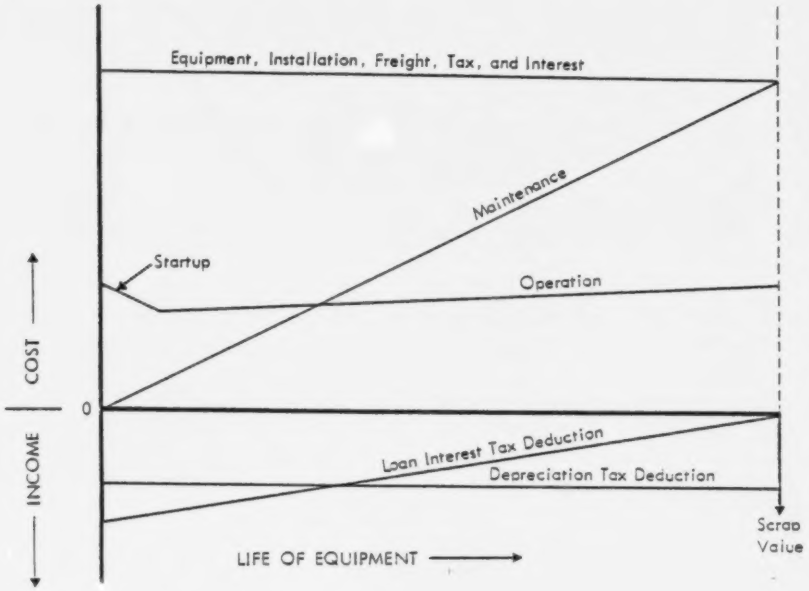

Figure 2. Graphical Presentation of Open Dust Control Costs.

The selection of one road dust control measure over another cannot rationally be determined on the basis of raw costs alone. The proper basis for comparison is the cost effectiveness which is defined as follows:

$$CE = \frac{D}{ER}$$

where:

CE = Cost Effectiveness ($/mass of emissions reduced)

D = Total Annual Expenditure ($/yr)

ER = Annual Emission Reduction (mass of emissions reduced/yr)

In the selection process, each candidate control measure should be analyzed to determine application parameters corresponding to its optimum cost effectiveness for the particular road segment(s) being considered. Finally, the control measure selected for implementation should be the one with the most favorable optimized cost effectiveness.

For example, the determination of optimum use of vacuuming of a particular paved road might include the following reasoning. The efficiency of vacuuming decays from the value at the time of application to zero as the surface dust loading builds up to its uncontrolled (equilibrium) value. Although the highest control efficiency would be achieved by continuous use of the available vacuum trucks, operating costs would be at a maximum. If the decay of control efficiency to zero consumed a period of 3 days, a single vacuuming of the road each day would produce about two-thirds of the maximum emission reduction at a fraction of the cost.

Clearly, the optimum cost effectiveness of vacuuming is a complex function of the mileage of road to be cleaned, the time it takes to pass over the road with the vacuum truck, and the rate at which the control efficiency decays after vacuuming. Mathematical cost effectiveness functions are being developed for each of the control measures tested, as part of this research program.

An approximate cost effectiveness value for a particular control measure may be estimated for one plant based on the value rigorously derived for another plant. The scaling procedure used for this purpose assumes that the optimal application frequency for a given control measure is independent of the application site. For example, the total cost of control per mile of road, as given in Table 5, may be used to estimate the cost of control of a road of specified length located at another plant by a simple multiplication.

CONCLUSIONS

The mean efficiencies of the control measures tested, except for vacuum sweeping of paved roads, were found to be independent of particle size. The fractional efficiency of vacuum sweeping decreased with decreasing particle size.

The mean control efficiency of Coherex® application to unpaved roads, which exceeded 90%, was substantially higher than the efficiencies of the other control measures tested. However, this efficiency reflected only the early stage in the expected lifetime of that control measure.

In the case of Coherex® application to unpaved roads traveled by light-duty vehicles, a well-defined initial decay in efficiency was observed. This is thought to reflect the buildup of surface dust loading on the treated road because of vehicular tracking of material from adjacent unpaved areas.

In the selection of the optimum control measure for a particular application, the proper basis for comparison is the cost effectiveness, which is defined as the total annual expenditure divided by the annual emission reduction. For each candidate control measure, cost information should be developed for several application scenarios, each with its associated control efficiency, and the optimum scenario identified. Finally the control measure selected for implementation should be the one with the most favorable optimized cost effectiveness.

ACKNOWLEDGMENT

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ENGLISH TO METRIC UNIT CONVERSION TABLE

English unit	Multiplied by	Metric unit
lb/vehicle mile	0.282	kg/vehicle km
lb	0.454	kg
mile	1.61	km

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2. Cowherd, Chatten, Jr., Russel Bohn, and Thomas Cuscino, Jr. Iron and Steel Plant Open Source Fugitive Emission Evaluation. EPA-600/2-79-103, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1979. 139 pp.

BLAST FURNACE CASTHOUSE CONTROL TECHNOLOGY - FALL 1981 UPDATE

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ABSTRACT

This paper describes blast furnace casthouse information that has become available in the past six months. Results of total mass and inhalable particulate testing on the baghouse inlet at Bethlehem Steel's Sparrows Point L furnace are presented. Baghouse outlet test data are also presented for Inland Steel's No. 7 furnace and Wheeling-Pittsburgh's Monessen No. 3 furnace. The status of United States and Canadian casthouse control systems as of September 1981 is provided along with a listing of world-wide controlled casthouses, excluding Japan. Cost data for installed systems are also given.

BLAST FURNACE CASTHOUSE CONTROL TECHNOLOGY - FALL 1981 UPDATE

INTRODUCTION

The number of blast furnace casthouse emissions control systems in the U.S. equalled nine by the Fall of 1981. Two of the controlled furnaces are new, modern, large furnaces (Bethlehem Steel, Sparrows Point "L" and Inland Steel No. 7), but the remaining seven systems are retrofits to older, smaller furnaces. Previously published papers have described existing systems and presented visible and mass emissions data.[1,2] Since publication of these two earlier papers, additional information has become available and will be presented herein.

The recent information includes total mass and inhalable particulate tests of ducted, baghouse inlet emissions at the Sparrows Point L furnace; baghouse outlet mass emissions tests at Inland Steel's No. 7 and Wheeling-Pittsburgh's Monessen No. 3 furnace; additional data describing U.S. Steel's efforts at the Edgar-Thomson Nos. 1 and 2 furnaces, and their experience with emissions suppression technology. Additionally, Dofasco has converted their Nos. 2 and 3 furnaces from total evacuation to local hood systems. Also summarized are cost data for each control option, indicating capital costs for installed systems and operating and maintenance costs.

The current trends in casthouse emissions control technology are focusing on local hoods and non-capture shrouding techniques. At present, only one blast furnace casthouse in North America is controlled by a total evacuation system - the No. 1 furnace at Dofasco.

CASTHOUSE CONTROL STATUS - UNITED STATES AND WORLD

Table 1 shows the status of casthouse control systems in the United States. By 1981, the American steel industry had made committments to government agencies to bring 128 (71%) of the approximately 180 standing blast furnaces into compliance by 1982. Of these 128 committments, 70 represent actual installation of control equipment. The remaining 58 furnaces are currently shutdown, or planned for shutdown before the end of 1982. These shutdowns are due to the retiring of older, smaller, less productive furnaces. As mentioned in previous papers, partial replacement of lost production will be accomplished by increasing the output of existing furnaces through techniques such as external desulfurization, modest hearth diameter increases during reline, burden and fuel improvements, installation of second tapholes, and increasing wind quantity and quality.

In summary, the American steel industry has made committments to install casthouse emissions control systems of 57 percent of the 122 blast furnaces currently planned for operation after 1982.

Blast furnace casthouse emissions were first controlled in the United States at a ferromanganese furnace at the Bethlehem Steel Corporation's

TABLE 1. U.S. CASTHOUSE CONTROL SYSTEMS INSTALLED AS OF FALL 1981

Plant	Furnace hearth diameter, ft-in.	Capture system[a]	Exhaust flowrate per fce., acfm	Retrofit or new, single or multiple tapholes
BSC/Johnstown[b]	-	TE	400,000	R/S
BSC/Bethlehem				
B	30-0	PE		R/S
C	27-11	PE	330,000[c]	R/S
D	30-0	PE	per fce.	R/S
E	24-0	PE		R/S
USSC/Edgar Thomson				
1	28-10	LH/NCS	140,000	R/S
2	28-10	NCS	None	R/S
Wheeling-Pittsburgh Monessen No. 3 (Jane)	28-0	LH	130,000	R/S
J&L Steel				
A-4[d]	29-0	NCS	None	R/S
H-3	32-0	NCS	None	R/M
C-3	30-6	NCS	None	R/M
BSC/Sparrows Point, L	44-6	LH	300,000	N/M
Inland Steel No. 7	45-0	LH	250,000	N/M

[a] TE = total evacuation; PE = partial evacuation; LH = local hoods; NCS = non-capture shrouding.

[b] Out of service since 1977.

[c] Total flow to baghouse is 660,000 acfm.

[d] Demonstration systems being refurbished; see text.

Johnstown Works in 1973. However, the first systems in the world were installed with the construction of new furnaces in Japan in the mid-sixties. The Japanese steel industry reported to EPA in 1976 that all furnaces at that time were either built with or retrofitted with various degrees of casthouse controls. Most Japanese retrofit systems are a combination of local hoods with the newer furnaces having canopy hood auxillary systems. The cleaning systems are predominantly baghouses, but scrubbers and electrostatic precipitators have also been used.

In the last few years the Japanese introduced another control option for blast furnace casting control. At the Kakogawa Works of Kobe Steel, one new furnace and two existing furnaces were fitted with roof monitor electrostatic precipitators. This system has no large fans or duct work and uses the natural bouyancy of the plume to move emissions through a wide plate electrostatic precipitator.

In Canada, both Stelco and Dofasco have experience with blast furnace casthouse control. Stelco's present experience is with a local hood control system on their new furnace at their Lake Erie Works and experiments with local hooding at the Hilton Works. Stelco plans to retrofit all four furnaces at the Hilton Works with local hooding.

Controls were retrofit to several West German blast furnaces between 1975 and 1980. Blast furnace casthouse controls have also been reported at facilities in Canada, Britain, Italy, France, Sweden, and the U.S.S.R. Table 2 summarizes available data for world-wide casthouse control systems. A partial listing of Japanese systems appears in Reference 3 which reports controlled furnaces operated by two Japanese steel companies.

MASS AND INHALABLE PARTICULATE TESTS AT THE BETHLEHEM STEEL L FURNACE

GCA measured total mass emissions and the particle size distribution in the ductwork serving the baghouse inlet at the L blast furnace at Bethlehem Steel's Sparrows Point plant in April 1981. The testing was sponsored by EPA's Industrial Environmental Research Laboratory as part of EPA's inhalable particulate (IP) measurement program.

CONTROL SYSTEM DESCRIPTION

Figure 1 illustrates one of the four identical emissions capture systems installed on each taphole and runner system at the L furnace. The iron trough and iron and slag runners are covered and evacuated at the following four points:

- notch-area local hood, 5 to 6 feet above the taphole,
- area encompassing the iron pool and dam (trough),
- area over the tilting iron runner, and
- area over the slag spoon.

TABLE 2. PARTIAL LIST OF CONSTRUCTED BLAST FURNACE CASTHOUSE CONTROL SYSTEMS IN THE WORLD[a]

Country	Plant	Furnace hearth diameter, ft-in.	Capture system[a]	Exhaust flowrate per fce., acfm	Retrofit or new, single or multiple tapholes
Canada	Stelco				
	Lake Erie	NA[b]	LH[c]	NA	N/M
	Hamilton	NA	LH	NA	R/S
	Dofasco				
	No. 1	20-9	TE[c]	325,000	R/S
	No. 2	20-9	LH	200,000	R/S
	No. 3	22-3	LH	200,000	R/S
	No. 4	28-0	LH	NA	R/M
West Germany	Krupp/Rheinhausen	37-9	LH	183,000	R/M
	Thyssen/Hamborn No. 4	37	LH	341,000	R/M
	Thyssen/Schwelgern No.1	45	LH	412,000	R/M
	Thyssen/Huttenbetieh No. 5	NA	LH	NA	NA
	Thyssen/Ruhrort No.6	NA	LH	NA	NA
	Mannesmann "A"	34	LH	421,000	R/M
	Mannesmann "B"[d]	34	LH	NA	NA
Sweden	Norrbottens Jarnverk AB, Lulea[e]	NA	LH	88,000	NA
Great Britain	British Steel Corp.				
	South Teeside No. 1	45-10	LH	338,000	N/M
	Llanwern	45-10	LH	NA	R/M
France	Usinor/Dunkirque No.4	46-8	LH	530,000	R/M
Italy	Italsider/Taranto No. 5	45-10	LH	353,000	N/M
USSR	Krivoy Roy/ Krivorozhstal No. 9	45	LH		N/M
	Krivoy Roy[d]	NA	LH		N/M
	Cherepovets	NA	LH		N/M
	Magnitogorsk	NA	LH		N/M

[a] Japanese systems not included; see Reference 3.

[b] NA = not available.

[c] LH = local hoods, TE = total evacuation

[d] Under construction.

[e] Reference 5

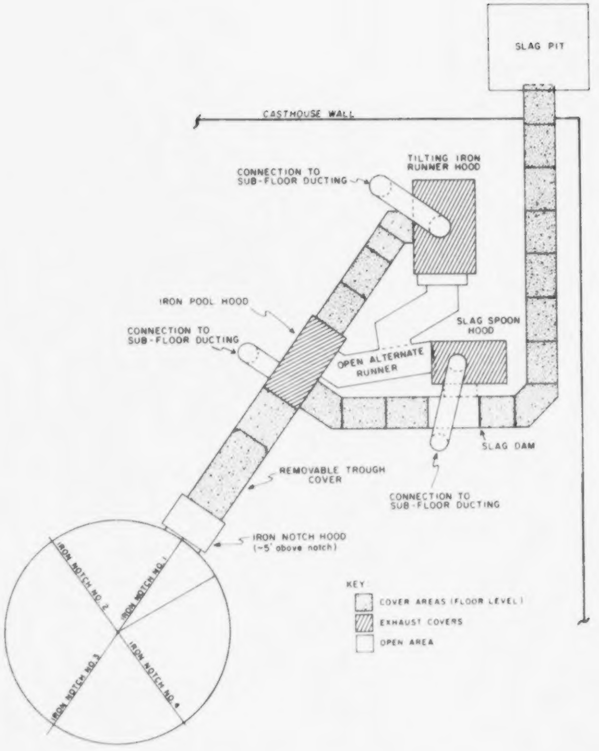
SLAG PIT
CASTHOUSE WALL
CONNECTION TO SUB-FLOOR DUCTING
TILTING IRON RUNNER HOOD
IRON POOL HOOD
SLAG SPOON HOOD
CONNECTION TO SUB-FLOOR DUCTING
OPEN ALTERNATE RUNNER
SLAG DAM
REMOVABLE TROUGH COVER
CONNECTION TO SUB-FLOOR DUCTING
IRON NOTCH HOOD (~5' above notch)
IRON NOTCH NO. 1
IRON NOTCH NO. 2
IRON NOTCH NO. 3
IRON NOTCH NO. 4
KEY
COVER AREAS (FLOOR LEVEL)
EXHAUST COVERS
OPEN AREA

Figure 1. Schematic of emission control system for "L" blast furnace at BSC/Sparrows Point (illustrated runner is typical of all four runners).

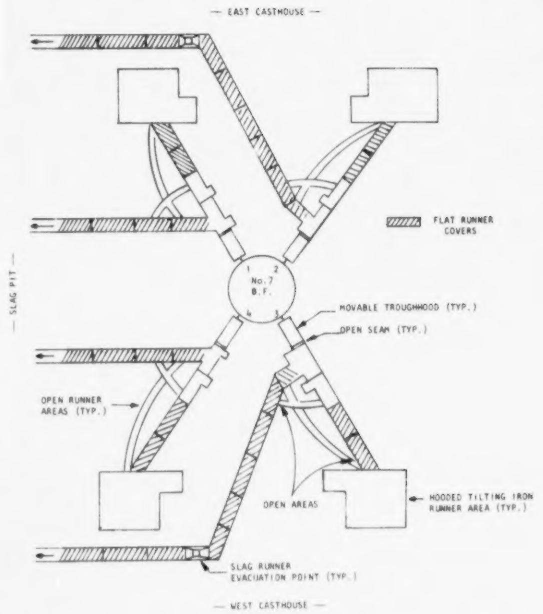
— EAST CASTHOUSE —
FLAT RUNNER COVERS
— SLAG PIT —
1 2
No. 7
B.F.
4 3
MOVABLE TROUGHHOOD (TYP.)
OPEN SEAM (TYP.)
OPEN RUNNER AREAS (TYP.)
OPEN AREAS
HOODED TILTING IRON RUNNER AREA (TYP.)
SLAG RUNNER EVACUATION POINT (TYP.)
— WEST CASTHOUSE —

Figure 2. Approximate sketch of No. 7 blast furnace casthouse layout. (Not to scale).

Total system exhaust flowrate measured during the tests averaged 320,000 acfm at 184° F. The flowrate applied to each exhaust point is not available at this time. The first section of the iron trough hood, adjacent to the taphole, is removed for drilling and plugging. All other sections of the exhaust system remain in place during casting with the exception of several small access doors that may be opened by workers.

Iron is alternately cast from two diagonally opposed tapholes for about one week before the off-line tapholes (and runners) are returned to service. Nos. 1 and 3 tapholes were operating during these tests. The exhaust system is sometimes used to exhaust notch-area hoods on the off-line runners to cool maintenance workers, although this only occurred for one 10-minute period during testing. Several casts overlapped during the field tests, i.e. two tapholes cast simultaneously. The overlap usually lasted for only 15 minutes, and testing was halted during overlap periods. Bethlehem stated that when casting two tapholes simultaneously, the ducts on both systems are fully opened and the exhaust capacity is approximately 50 percent on each.

Captured emissions are controlled by a Wheelabrator-Frye positive pressure baghouse, with a design capacity of 312,000 acfm at 140° F. The five chamber baghouse operates with one chamber always in a cleaning cycle (shaker), resulting in a net air/cloth ratio of 2.5:1. Compartment ΔPs ranged from 2 to 6 inches H_2O during the evaluation.

MASS, INHALABLE AND VISIBLE EMISSIONS DATA

Four EPA Method 5 test runs were conducted on 28 and 29 April 1981 during casting (iron and slag flow). Three to four Andersen impactor runs were conducted during each Method 5 test. Table 3 summarizes the test results. Testing did not include drilling and plugging emissions and also excluded clean-up operations that occur after taphole plugging. Testing was halted for a few periods of casting overlap when the exhaust flow was divided between two tapholes. Individual Andersen impactor test runs are not shown in Table 3 since the IP test protocol recommends averaging of all size data for a more accurate, single number. Also shown in Table 3 are available process data describing casting conditions during test periods.

Method 9 opacity observations of visible emissions escaping capture and exiting casthouse roof monitors during testing showed the following results for 8.5 hours of observation:

- 7.1% of Method 9 observations were $\geq$20% opacity
- 1.1% " " " " $\geq$40% "
- 0.5% " " " " $\geq$60% "

One additional hour of observations are not included in the above summary because interference from another process precluded observation of the roof monitor. Table 4 compares roof monitor visible emissions with process operations. All roof monitor emissions greater than 10 percent opacity resulted from drilling, taphole lancing, plugging, and overlapping casting. During single taphole operations, most roof monitor emissions (excluding drilling and plugging)

TABLE 3. SUMMARY OF MASS AND IP TESTS AT THE L FURNACE

Run Number	Total Mass Emissions (Baghouse Inlet),[a] lb/ton iron	Mass <15μm,[b] lb/ton	Mass <2.5μm,[b] lb/ton
1	1.21		
2	1.36	(Individual impactor runs not reported-see text)	
3	1.40		
4	1.21		
Average	1.3	0.27	0.17

Hot metal sulfur, average 0.024, wt. percent
Hot metal temperature, average maximum - 2740°F
average at slag over - 2692°F

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[a] Final results.

[b] Preliminary results.

TABLE 4. COMPARISON OF VISIBLE EMISSIONS ESCAPING THE CASTHOUSE TO PROCESS OPERATIONS, "L" BLAST FURNACE, 27-29 APRIL 1981

Operation	Visible emissions, % opacity		Typical duration of operation (min)
	Typical	Range	
Drilling and O_2 Lancing	15-20	0-60	2-3
Single cast[a] (full evacuation)	0-5	0-10	100-115
Overlapping cast[a,b] (partial evacuation)	10-15	0-30	10-15
Plugging	20-40	5-90	5-7

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[a] Excluding drilling and plugging emissions.

[b] Emissions shown are for whichever casthouse showed the highest emissions during simultaneous casts.

originated from an opening in the slag runner cover used for slag working. The small access door on this opening had apparently been removed in order for workers to gain access to the slag surface.

INSHOP EMISSIONS OBSERVATIONS AND PROCESS DATA

The inshop process observer assessed the origin and magnitude of emissions escaping capture using the following criteria:

- Light emissions - those appearing to be in the 5 to 25 percent opacity range as viewed by the inshop observer,
- Moderate emissions - those appearing to be in the 30 to 60 percent opacity range, and
- Heavy emissions - those appearing to be of 65 to 100 percent opacity.

Table 5 briefly summarizes inshop emissions observations, as recorded by the process observer stationed on the casthouse floor.

The inshop observer estimated that the notch hood captured approximately 90 to 95 percent of drilling emissions and 70 to 80 percent of oxygen lancing emissions. Uncaptured lancing emissions observed inside the shop were generally in the moderate to heavy range, while drilling emissions were usually light.

Once the iron trough hood was in place, emissions escape from the system was usually zero, except during simultaneous casting. When slag flow began, light emissions escaped the slag spout hood opening as mentioned previously. During plugging, the notch-area hood appeared to capture roughly 40 to 50 percent of the emissions.

SUMMARY OF OTHER RECENTLY AVAILABLE INFORMATION

Since preparation of the two previous papers, additional information has become available for several existing control systems. The following paragraphs update previously published information, and present some new data. Refer to the earlier papers for a complete technology overview and background information for systems discussed below.[1,2]

BAGHOUSE OUTLET TESTS AND PROCESS OBSERVATIONS AT INLAND STEEL'S NO. 7 FURNACE

Compliance tests of the baghouse outlet stack serving the casthouse control system at Inland Steel's new No. 7 blast furnace were conducted on 27 March 1981. The three test runs reported to EPA showed outlet grain loadings of 0.0042, 0.0059, and 0.0069 gr/dscf for a test average of 0.0057 gr/dscf. Two

TABLE 5. INSIDE CASTHOUSE EMISSIONS ASSESSMENTS, "L" BLAST FURNACE, 28-29 APRIL 1981[a]

Operation	Emissions magnitude				
	Notch area	Iron trough	Dam hood	Iron Spout hood	Slag Spout hood[b]
Drilling	L-M	L-M	0	0	0
O_2 lancing	M-H	M-H	0	0	0
Single cast (full evacuation)	0	0	0	0	L-M
Overlapping cast (partial evacuation)[d]	L	0-L	L-M	0-L	L
Plugging[e]	H	H	0	0	L

[a] Assessment technique using L (Light), M (Moderate), and H (Heavy); see text.

[b] Emissions only when slag was running (∿50% of total cast time).

[c] Three of six drill periods observed were oxygen lanced.

[d] Data for casthouse showing highest emissions.

[e] Partial notch-area evacuation due to simultaneous casting occurred for two of six plugs included here.

TABLE 6. ROOF MONITOR VISIBLE EMISSIONS DATA FOR WHEELING-PITTSBURGH'S MONESSEN NO. 3 CASTHOUSE

Test Period	No. of Casts Observed	Total Method 9 Observations	% of Total Method 9 Observations		
			≥20%,	≥40%,	≥60%
EPA Demonstration	50	12,837	7.25	1.78	1.04
Company data after improvements	61	N/A[a]	2.8	N/A	<0.1

[a] Not available.

tests were apparently conducted during overlapping casts (two tapholes cast simultaneously). The system exhaust flowrate varied about five percent between test runs, averaging 255,000 acfm at 115° F.

Roof monitor visible emissions observations conducted during daylight portions of the tests showed that 0.3 percent of the Method 9 observations were greater than or equal to 20 percent opacity. Simultaneous inshop observations found that all roof monitor emissions occurring during casting were caused by taphole plugging.

The No. 7 furnace is very similar to the L furnace at Sparrows Point with respect to both furnace design and emissions control system layout (see Figure 2). However, the notch-area hood at Inland consists of hooding above and along both sides of the taphole, while the notch-area hood at the L furnace consists of a single, horizontal hood above the taphole. Another similarity between Inland's No. 7 and Bethlehem's L furnace is that when two tapholes are cast simultaneously, the available exhaust flow is split nearly equally between each taphole system.

Observations of four casts inside the No. 7 furnace during the stack tests noted that during main cast periods (including slagging), only minor puffs escaped capture, quickly dissipating to zero percent opacity within the casthouse. Approximately 95 percent of drilling emissions and most plugging (and iron trough hood removal) emissions were estimated to be captured by the notch-area hoods. Observation of two-taphole casting from inside the No. 7 casthouse found that emission escape from hoods and runner systems was essentially unchanged from single cast operations.

UPDATE OF CASTHOUSE CONTROL EFFORTS AT DOFASCO

As reported previously, Dofasco converted the total evacuation systems on their Nos. 2 and 3 blast furnaces to local hoods in late 1980 and 1981. Both furnaces now have two tapholes. By the summer of 1981, notch-area hoods, currently exhausting at about 150,000 acfm (per furnace), were installed on both furnaces. Local hoods were also installed on iron spouts on the No. 3 furnace, exhausting about 50,000 acfm from the ladle in use. Dofasco-designed runner covers were installed on the iron and slag runners of both casthouses. Dofasco plans to complete the two systems by mid-1982 with addition of local hoods on iron ladle spouts at the No. 2 casthouse, and installation of a new "third-generation" runner cover design on both casthouses. The runner covers are based on the non-capture, supression concept. The Nos. 2 and 3 furnaces can now be cast simultaneously with controls, since total exhaust flow rate under simultaneous casting is 400,000 acfm, the capacity of the existing baghouse. With the old total evacuation system sized at 400,000 acfm per casthouse, both furnaces could not be controlled simultaneously.

Local hoods were at one time being considered for the totally-evacuated No. 1 casthouse. However, an improved, stainless steel seal between the furnace shell and the bustle pipe was installed during the summer 1981 reline. The company reports that the new seal is effective in controlling emissions escape from this critical area, and Dofasco plans to continue total evacuation control of the No. 1 furnace.

The local hood and runner cover system that is partially complete on Dofasco's No. 4 furnace is scheduled for completion by August of 1983.

WHEELING-PITTSBURGH MONESSEN NO. 3 UPDATE

The Wheeling-Pittsburgh system consists of an iron trough hood and two iron spout hoods, evacuated to a baghouse. The trough hood is approximately 27 feet long, extending four feet past the dam. The trough hood is constructed in two sections so the 15 foot long forward (taphole) section can be removed by the shop crane to facilitate work around the trough area. The height of the hood bottom, above the casthouse floor, is about five to six feet. The two iron spout hoods measure about five feet square and have a steel pipe curtain around the hood perimeter, extending to the top of the hot metal ladle (U.S. Patent No. 4,245,820).

During casting, the trough hood and one iron spout hood are evacuated at a design flowrate of 140,000 acfm (total system). When the first ladle is full, iron flow and hood exhaust flow are diverted to the second iron spout. The exact flowrate for each hood is not available at this time. Figures 3 and 4 illustrate the layout of the Monessen system.

The demonstration test of roof monitor visible emissions from the Wheeling-Pittsburgh Monessen No. 3 local hood system was completed in April 1981. Comparison of inside and outside observations indicated that most emissions leading to roof monitor visible emissions $\geq$20 percent opacity came from the uncontrolled slag runners and slag spout, and to a lesser extent, the iron runners. Since the test period, Wheeling-Pittsburgh has been refining their system and investigating additional techniques for reducing emissions. Specific areas of improvement to date are: 1) changing slag runner material, 2) installing additional cross-wind barriers and 3) lowering the bottom edge of the iron trough hood by one or two feet. Table 6 summarizes the results of the EPA-sponsored demonstration test of 50 casts, and the more recent company-supplied data showing results of the improvements made since the EPA tests.

Method 5 tests were recently conducted on one of the 10 stub stacks serving the 10 compartment baghouse on the Monessen No. 3 furnace. Three test runs showed outlet grain loadings of 0.0016, 0.0017, and 0.0023 gr/dscf, for an average of 0.0019 gr/dscf. Since only one compartment was tested, the total control system flow rate could not be measured.

U.S. STEEL, EDGAR THOMSON UPDATE

Preliminary evaluation of the Edgar Thomson No. 1 system was conducted in July 1981. Final evaluation of the system by U.S. Steel and EPA will not be completed for several months.

The Edgar Thomson No. 1 furnace is fitted with a local hood above the iron trough, measuring about 16 feet in length from the taphole. The hood covers the first 60 percent of the trough area, and is evacuated at 140,000 acfm through two ducts, located behind and in front of the bustle pipe. The

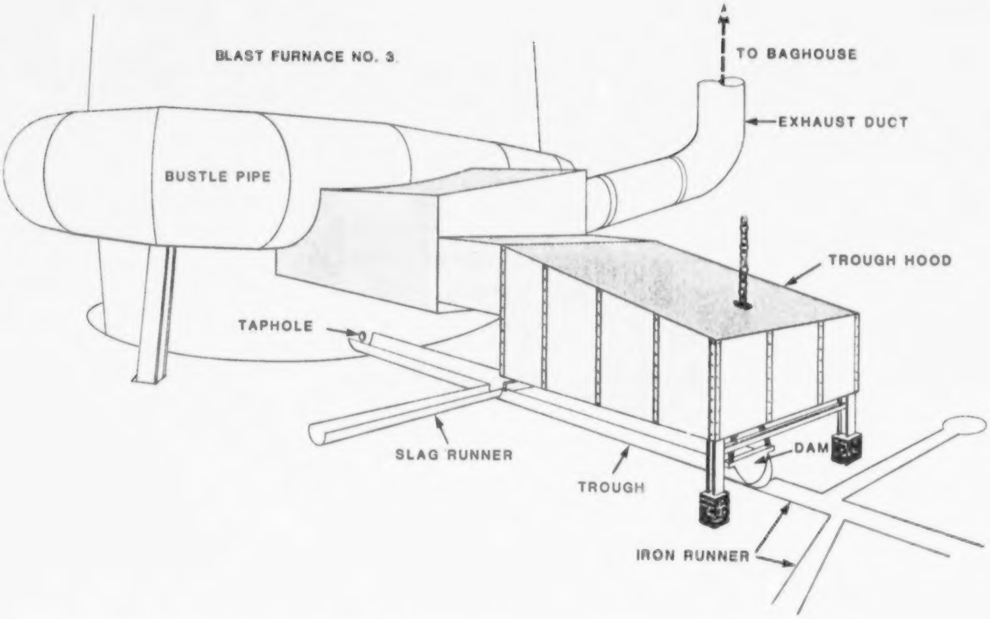
BLAST FURNACE NO. 3
TO BAGHOUSE
EXHAUST DUCT
BUSTLE PIPE
TROUGH HOOD
TAPHOLE
DAM
SLAG RUNNER
TROUGH
IRON RUNNER

Figure 3. Isometric View of Trough Hood at Wheeling-Pittsburgh, Monessen No. 3. (Courtesy of JACA Corporation)

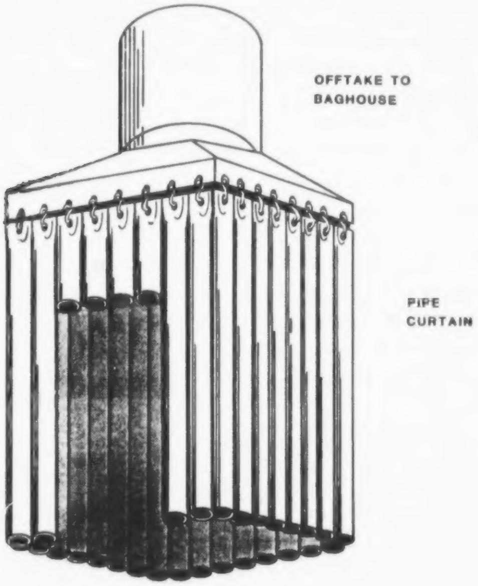
OFFTAKE TO BAGHOUSE
PIPE CURTAIN

Figure 4. Isometric View of Hot Metal Ladle Hood (Pipes Enlarged to Show Detail), at Wheeling-Pittsburgh, Monessen No. 3. (Courtesy of JACA Corporation)

lower edge of the hood lies 11 to 12 feet above the casthouse floor. The hood exhausts to a baghouse.

An inverted U-shaped air curtain, fitted with a number of horizontal air jets along the U-shaped perimeter, is located about 10 to 15 feet from the dam. The air curtain device is designed to push skimmer and trough area emissions into the hood, a so-called "push-pull" system. Rated at 4700 acfm, the air curtain can be throttled down to provide the proper push/pull effect.

The remainder of the No. 1 casthouse is fitted with J&L-type non-capture suppression technology. The No. 2 furnace at the Edgar Thomson Works is entirely fitted with J&L-type technology (no fans or baghouse). As in the case with the No. 1 system, final company and EPA evaluation of the No. 2 system is not yet complete.

J&L'S NON-CAPTURE TECHNOLOGY UPDATE

The three J&L prototype systems used for last year's EPA demonstration tests are not presently in service. J&L is constructing permanent versions of these systems and modifying the control systems, furnaces, and casthouses to improve performance. J&L reports that the permanent systems will enter service on furnace C-3 at Cleveland, A-4 at Aliquippa, and H-3 at Indiana Harbor. The H-3 furnace was not used in the demonstration test, but will be fitted with the permanent system because the furnace is currently down and can be more easily retrofit than the (operating) H-4.

U.S. STEEL'S NON-CAPTURE, EMISSIONS SUPPRESSION EXPERIMENTS

U.S. Steel is experimenting with non-capture suppression techniques that differ from the J&L technology. Development work is underway at the No. 2 blast furnace at the Geneva, Utah plant. No formal evaluation of the system has been conducted by EPA. Additional details are not available because U.S. Steel considers this a proprietary system and has exerted a confidentiality claim on their work.

AVAILABLE COST DATA

The cost of controlling blast furnace casthouse emissions will vary depending on such factors as furnace production size, ease of retrofitting the control system, type of control system selected (amount of exhaust air to be moved), emissions characteristics of the furnace, and the overall effectiveness of the system after installation. The cost figure can be divided into two basic categories - capital cost, and annual utility (operating) plus maintenance costs (O&M). These two components can vary for two identical furnaces with the same control option located at separate plants based on retrofit difficulty, number of common systems (shared baghouses), and the local cost of power.

Table 7 summarizes cost data for installed systems, as provided by each company. The origin and basis of each cost is discussed below.

TABLE 7. SUMMARY OF AVAILABLE COST DATA[a]

Company	Blast Furnace	Capture[b] System	Capital Cost, x10^6	O&M Cost, per year, x10^3
Dofasco	Nos. 2&3	Total Evacuation	8.3[c]	-
	No. 1	Total Evacuation	-	144
Bethlehem, Bethlehem	B,C,D,E	Partial Evacuation	11.4[d]	375[e]
Wheeling-Pittsburgh, Monessen	No. 3	Local Hoods	1.9	100-150[f]
J&L Steel	2500 tpd furnaces	Non-Capture	0.75-1.15[g]	130[g]

[a] All cost data in 1981 American dollars.

[b] All systems use baghouses for gas cleaning, except J&L technology.

[c] Cost for two furnaces, with single baghouse.

[d] Cost for four furnaces, with a single baghouse. Includes costs incurred during original study on E furnace; part of equipment salvaged for final construction.

[e] Based on annual operation of two and one-half furnaces.

[f] Company rough estimates vs. actual costs for all other data.

[g] J&L's estimate for 2500 tpd furnace.

DOFASCO - TOTAL CASTHOUSE EVACUATION

Dofasco reported that the total building evacuation system installed on their Nos. 2 and 3 blast furnaces at the Hamilton Works cost $1,100,000 for curtain walls, $2,800,000 for duct work, and $2,500,000 for the baghouse and fan.[4] This total of $6,400,000 (Canadian dollars) was calculated to be equivalent to $8,270,000 in March 1981 dollars, using the Chemical Engineering Plant Cost Index. Using 18 percent interest amortized for 20 years, the annual captial cost is approximately $1,500,000.

For the similar total building evacuation system on Dofasco's No. 1 furnace, annual operating costs of $74,000 for electrical power and $22,000 for maintenance were reported. For that furnace, the annual operating cost would be $96,000 per year (1978 Canadian dollars). Assuming that costs increased 30 percent from this period and assuming the same U.S./Canadian conversion rate of 15 percent, Table 7 shows 1981 O&M cost estimates.

BETHLEHEM STEEL - PARTIAL EVACUATION

Bethlehem Steel Corporation (BSC) indicated that the capital cost of the four partial evacuation systems installed in their Bethlehem Works in 1980 was $10,400,000 (including costs incurred during original study on E furnace). BSC also stated that the annual operating and maintenance costs when two and one-half furnaces are operating is $375,000 (averaged over the year). Updated to March 1981 dollars, the installed capital cost is approximately $11,400,000. It should be noted that this is a high flow, partial evacuation system with all four furnaces sharing a common baghouse. BSC reported that the capital cost figure includes the spacing problem for the single baghouse and the large diameter, long run ductwork with substantial supporting.

WHEELING-PITTSBURGH - LOCAL HOODS

The recent installation of a local hood system at the Wheeling-Pittsburgh Monessen Works No. 3 blast furnace was reported to cost approximately $1,900,000 in 1981 dollars. Although O&M costs have not yet been reported, the company's rough estimate is in the range of $100,000 to $150,000 per year. Amortizing this capital cost over 20 years and assuming a mid-range O&M cost shows an annual cost of $342,000 for capital and $125,000 for O&M. Wheeling-Pittsburgh plans to use this baghouse with additional modules when they install local hooding systems on the other furnaces, to help reduce baghouse capital costs.

J&L STEEL - NON-CAPTURE SHROUDING

The system that shows the greatest potential to date for reducing the cost of blast furnace casthouse controls is the non-capture shrouding technology demonstrated by J&L Steel. J&L markets this technology and requires licensing fees. The fees quoted by J&L are $50,000 to review the system at a J&L plant, $150,000 to receive the complete engineering package, technical know-how, and license for one taphole, and finally, $50,000 for the license for each additional taphole. J&L's current estimate is $750,000 in capital cost for a single taphole furnace with the slag spouts outside the arcade, and $1,150,000 for a single taphole furnace with the slag spouts inside the arcade.

J&L's estimated operating cost is $0.15 per ton of hot metal which translates to about $130,000 per year for O&M for a 2500 tpd, single-taphole furnace. J&L's current installations are on furnaces of 2,200, 2,750, and 3,000 tpd. J&L also reports that these three furnaces, used for the EPA demonstration tests, experienced a one percent increase in hot metal yield as a result of using the non-capture emissions control system. Also experienced was an increase in the temperature of hot metal delivered to the BOF shop.

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COKE QUENCH TOWER EMISSIONS AND EMISSIONS CONTROL

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ABSTRACT

Available test data indicate that the mass of particulate emissions from a coke quench tower may be affected by quench water quality (based on dissolved or total solids in the quench water), and the design and location of baffles in the tower. This paper examines the impacts of the water quality and baffle design on quench tower emissions and emissions control. Emissions test data and engineering models are used to estimate the relationship of these parameters to emissions. Six possible control schemes are defined and the impacts of the controls are evaluated.

INTRODUCTION

Over the past decade emissions from coke quench towers and the development and evaluation of control measures for these emissions have drawn increased attention from both air pollution control agencies and industry personnel. Prior to 1976, concerns about quench tower emissions centered on the compliance of specific towers with state and local regulations. In 1976, the U.S. Environmental Protection Agency (EPA) conducted extensive tests at the U.S. Steel Corporation's Lorain, Ohio plant. The results of these tests brought added attention to the problems of quench tower emissions. Over the past 3 years, interest in quench tower emissions has heightened as different offices within EPA have: (a) considered a new source performance standard for wet coke quenching; (b) issued Reasonably Available Control Technology (RACT) guidelines for coke quench towers; and (c) evaluated coke quench towers as one of the major sources of inhalable particulate emissions in the iron and steel industry. These activities have resulted in a number of emissions tests and comprehensive data analyses that have significantly increased our knowledge of quench tower emissions. Many of the results were summarized in a recent paper by Bloom and Jeffery[1] and are described in more detail in an earlier study by Gorman, et al.,[2] and in a recent EPA study.[3]

While our understanding of quench tower emissions and emissions control have increased greatly in the last 10 years, questions are still unanswered. In their paper, Bloom and Jeffery[1] identify a number of factors related to tower and baffle design, water quality, and operating characteristics which might affect quench tower emissions and emissions control. In addition, they identify existing data needs related to back-half particulate composition (i.e., the composition of particulate captured in the impingers of an EPA Method 5 sampling train), the relationship of quench water and makeup water quality, particle size distribution, and particulate generation mechanisms.

This paper will address the impacts of two of these parameters, water quality and baffle design, on quench tower emissions and emissions control. Bloom and Jeffery[1] found that for a large number of tests under a variety of process conditions the front-half particulate emissions (those emissions capture on or prior to the filter in an EPA Method 5 sampling train). are proportional to the dissolved solids in the quench water lost up the stack. Although these results (see Figure 1) are strongly influenced by the tests from U.S. Steel-Lorain, they found that a regression line through the data from U.S. Steel-Gary and DOFASCO had almost the same slope. These data suggest that emissions are related to the product of the spray water solids concentrations and the quantity of water emitted from the tower. Data further suggest that the quantity of water lost up the stack is dependent on baffle design.

Both of these parameters have potentially significant impacts on quench tower emissions, and control of the parameters is feasible. This paper reviews the current state of knowledge and identifies major data gaps related to the relationship of water quality to quench tower emissions and the performance of different baffle systems, control schemes involving water quality control and baffling, and potential secondary impacts of these control schemes.

IMPACT OF WATER QUALITY ON QUENCH TOWER EMISSIONS

RELATIONSHIP BETWEEN QUENCH WATER SOLIDS AND PARTICULATE EMISSIONS

The nature of the quenching operation, given the quantities of water vapor and droplets lost up the stack, strongly suggests that the quantity of particulate emissions from quench towers will be related to the quantity of solids in the water sprayed onto the coke. This relationship was first demonstrated in the analysis of test data from U.S. Steel-Lorain, Ohio, by

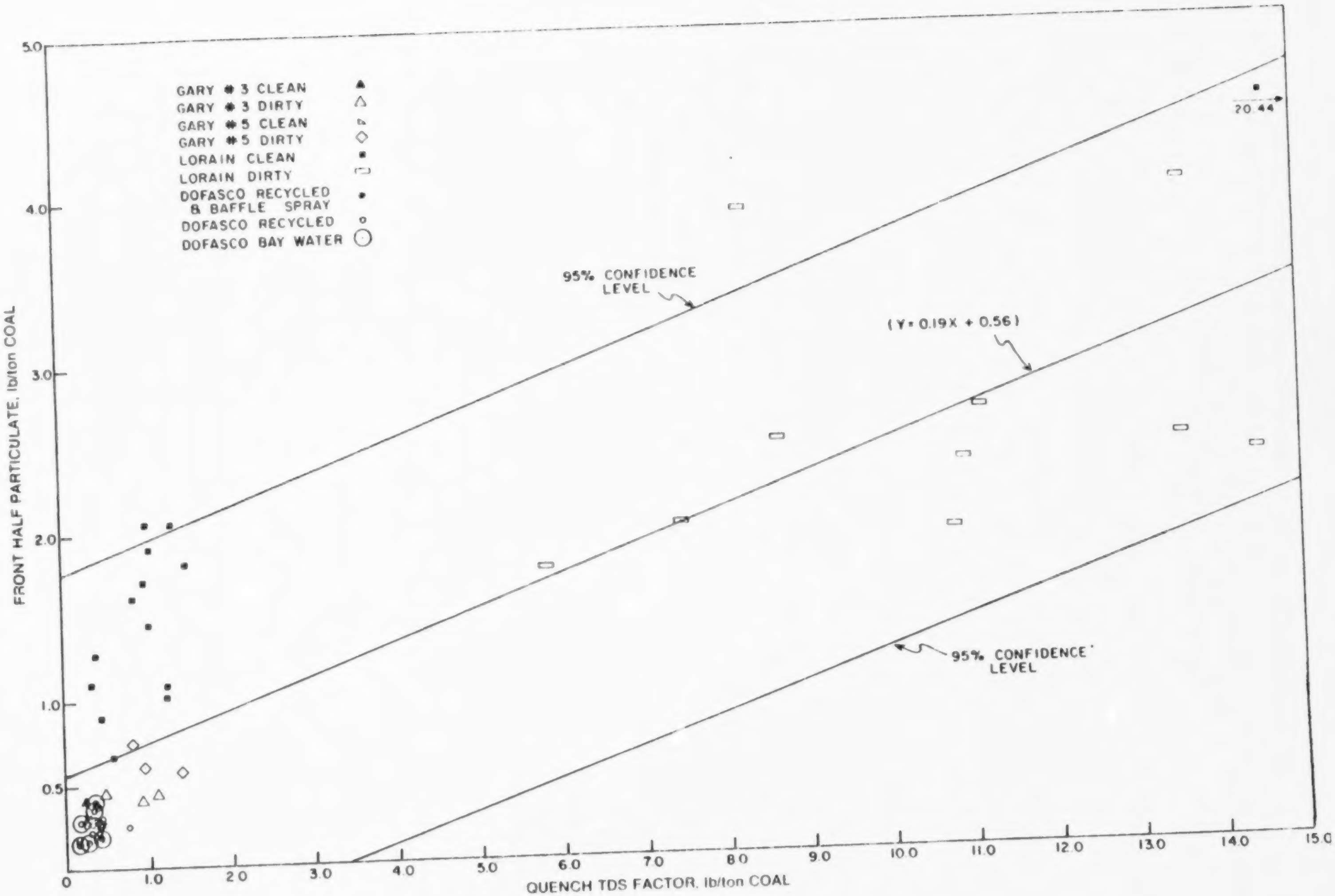


Figure 1. Front half particulate, lb/ton coal.

Edlund, et al. Those initial tests suggested a relationship between particulate emissions and total dissolved solids (TDS) in the quench water demonstrated by the regression equation:

$$E = 0.18\ DW \times 10^{-6} + 1.0 \qquad \text{Eq. 1}$$

where E = particulate emissions (kg/Mg of coke)
D = dissolved solids in quench water (mg/ℓ)
W = water lost up the tower during quenching (ℓ/Mg)

This relationship was substantiated by Bloom and Jeffery[1] who found that for a number of different towers (see Figure 1) the emissions are related to TDS by the equation:

$$E = 0.19\ DW \times 10^{-6} + 0.40 \qquad \text{Eq. 2}$$

where the variables are defined as above.

Note that, in both of the above analyses, emissions from the quench tower were compared to a quench water solids factor that combined the concentration of TDS in the quench water and the quantity of water lost up the stack. In order to isolate the impact of solids concentration, these same tests were used to compare particulate emissions to the concentration of total solids (both dissolved and suspended). Total solids (TS) was chosen as a parameter because it is likely that the mechanisms which lead to the emission of TDS will also lead to the emission of suspended solids. Hence, total solids concentration may better indicate the impact of water quality on emissions.

The results of the analysis are shown in Figures 2 and 3. Figure 2 represents the results for quench towers having single row baffles. For both sets of test data (U.S. Steel-Lorain and U.S. Steel-Gary, Tower No. 5) the results suggest a linear relationship between particulate emissions and the concentration of total solids in the quench water. Both slopes were found to be statistically significant at the 5% level. Using the average data from tests at these two towers, emissions were found to be related to total solids concentration by the equation:

$$E = 1.46 \times 10^{-4}(TS) + 0.43 \qquad \text{Eq. 3}$$

where E = emissions (kg/Mg)
TS = total solids concentration in the quench water (mg/ℓ)

Figure 3 presents the results for three towers with multiple row baffles. The slope of this line is quite small, suggesting that little relationship may exist between total solids concentration and emissions over the range of solids concentration tested (300 to 2,000 mg/ℓ). However, the slope of the line was not found to be statistically significant, and the results are for a narrow range of total solids concentrations. Further data are needed to evaluate the impact over a wide range of solids concentrations.

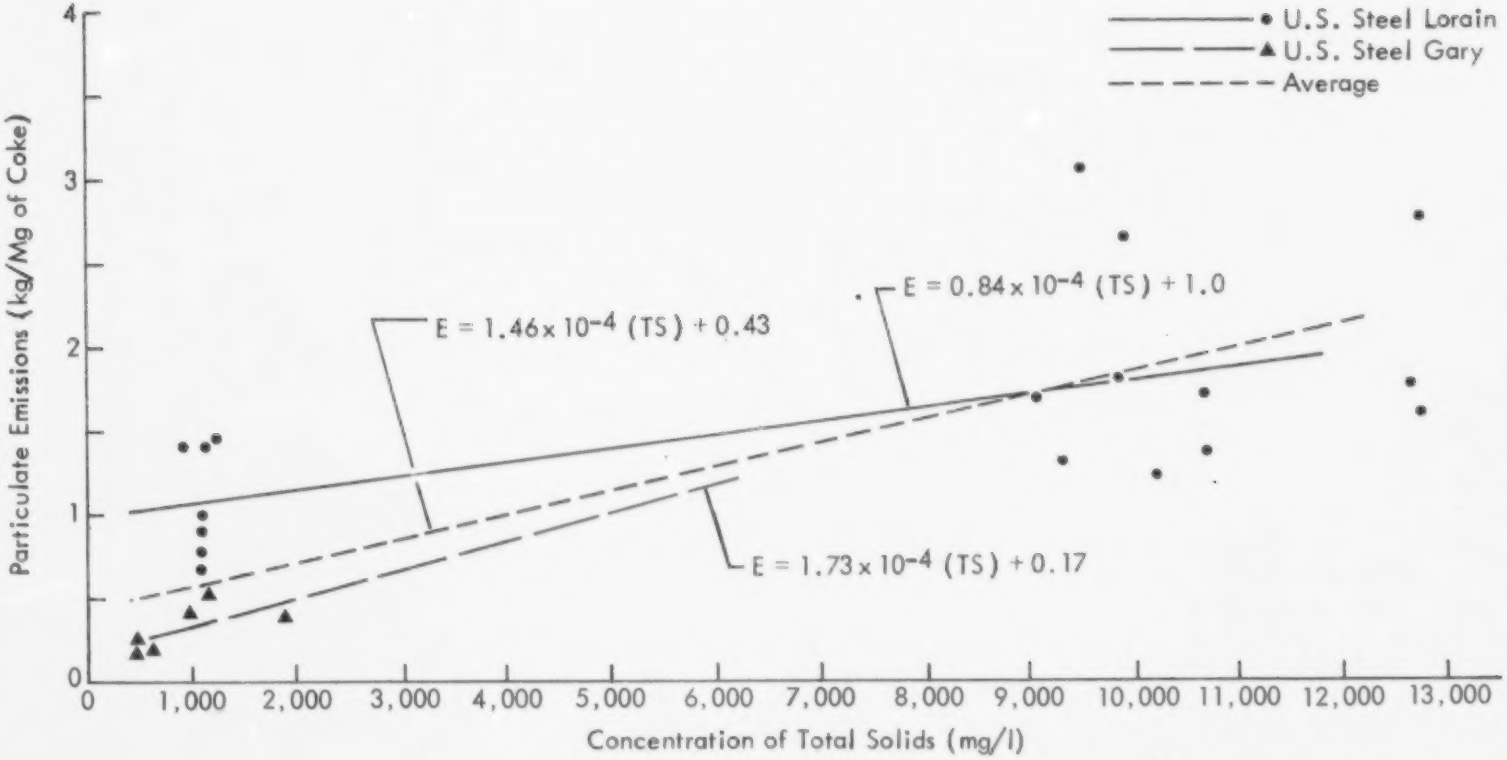


Figure 2. Relationship of particulate emissions to quench water solids concentrations for towers with single row baffles.

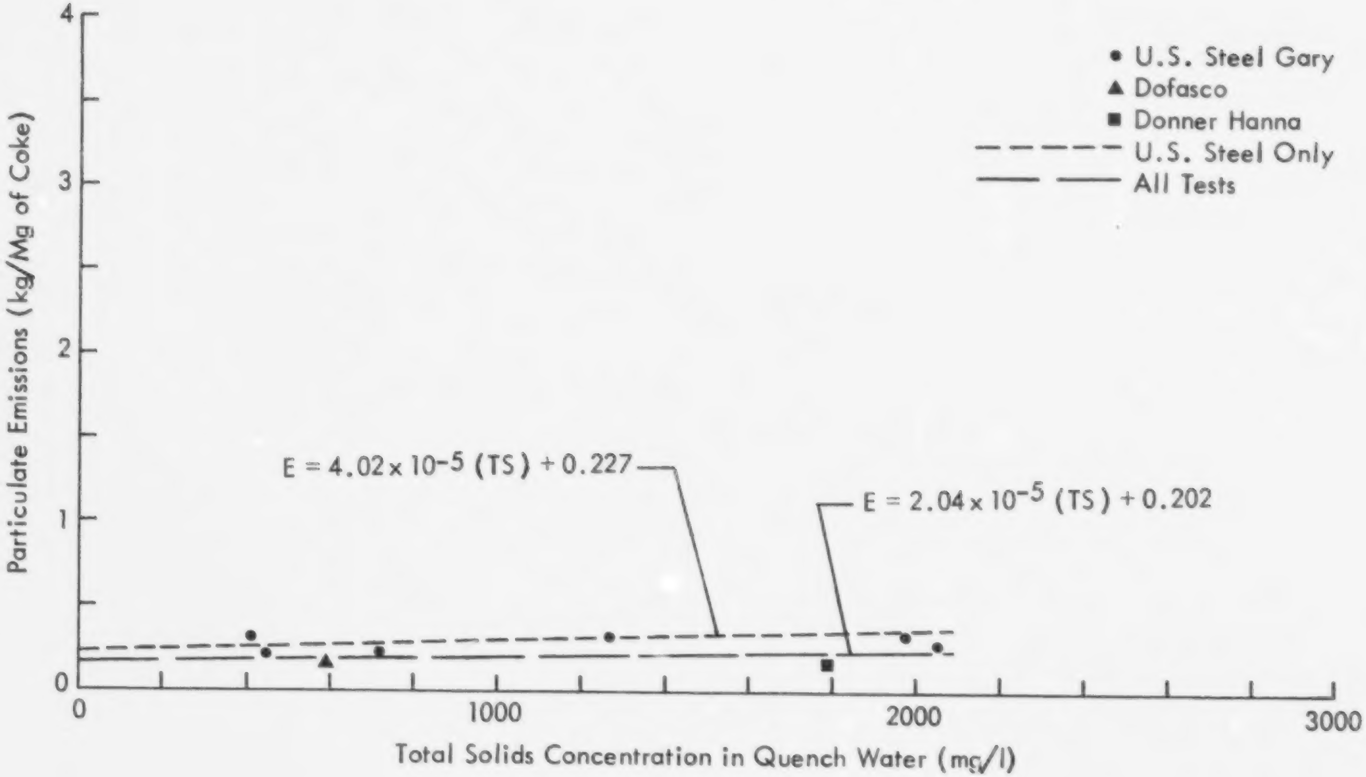


Figure 3. Relationship of Particulate Emissions to quench water solids concentrations for towers with multiple row baffles.

In summary the test data suggest that, for towers with single row baffles, particulate emissions can be reduced by controlling the quantity of solids in the quench water. However, note that with respect to suspended solids the conclusion is weak, in that for all available tests the quantity of suspended solids was minor in comparison to the quantity of dissolved solids. Over the range of total solids concentrations (300 to 2,000 mg/ℓ), no statistically significant relationship was found between particulate emissions and quench water solids for composite data for towers with multiple row baffles. Future testing may provide a clearer understanding of this relationship.

CONTROL OF QUENCH WATER SOLIDS

In the typical quenching process, water is pumped from a sump to a holding tank and then supplied to the spray nozzles by gravity flow. As the water is sprayed onto the hot coke, about 25 to 30% is "removed" from the quench tower by one of three paths: (1) the water is evaporated and carried to the atmosphere as vapor; (2) droplets are captured in the quench tower draft and exhausted to the atmosphere; and (3) the water is carried out in the quench car as moisture in the coke. Most water is lost via the first two pathways. The water that is not lost is captured and recirculated to the holding tank through the sump. Makeup water is added to the sump to replace that which is lost from the sump.

Solids can be added to the quench water at two points in the cycle: from the coke to the sump return water or with the makeup water. Data indicate that few added solids enter the system with the return water. In fact, in most cases the concentration of total solids in the return water is less than that in the quench water. Control of these solids beyond that typically practiced is unlikely in that dissolved solids in the return water cannot reasonably be controlled, and most added suspended solids are now controlled by settling in the sump.

The primary source of solids in the quench water and the source which is most amenable to added control is the makeup water to the sump. Potential sources of makeup water for the quench tower include the various effluent streams from the by-products plant, blowdown from process cooling waters, blowdown from wet scrubbers used for charging or pushing control, and local surface or ground waters. The solids concentrations of these streams and the quantities of water available for makeup are shown in Table 1. For process waters, the table also shows the potential incremental increase in emissions that can be expected from the use of process waters rather than natural water sources. These estimates are based on Equation 1 and the assumptions that all makeup water is eventually emitted from the tower and that total solids in natural water sources average 300 mg/ℓ. The data in Table 1 suggest that the sources of makeup water which potentially have a major impact on quench tower particulate emissions are the excess ammonia liquor stream (sometimes called flushing liquor or weak ammonia liquor) and blowdown from coke plant scrubber systems.

TABLE 1. SOURCE OF QUENCH TOWER MAKEUP WATER

Water source	Quantity of water available for quenching ℓ H_2O/Mg coke[a]	TDS (mg/ℓ)	TSS (mg/ℓ)	Potential[k] Incremental Emissions Contributions (kg/Mg)
Excess ammonia liquor	79-430 (158.2)	15,875[b]	59[c]	0.50
Final cooler blowdown:				
Once through	46-625 (378)[i]	262.2[d]	40[c]	< 0.001
Recirculate	8.3-42 (38.3)	840[e]	40[c]	0.004
Benzol plant:				
Once through	625	1,054[b]	67[c]	0.10
Recirculate	63-500 (71.6)	1,054[b]	67[c]	0.012
Barometric condenser:				
Once through	83-625 (625)[i]	NA	NA	-
Recirculate	12-42 (46)	NA	NA	-
Scrubber blowdown:				
Charging	198[f]	450[j]	3,202[j]	0.13
Pushing	625[f]	450[e]	3,202[e]	0.42
Other noncontact cooling:				
Water blowdown	625	510[e]	32[e]	0.030
Natural water sources:				
Lake Erie	625	170[g]	NA	-
Lake Michigan	625	160[g]	NA	-
Ohio/Mahoning River (avg.)	625	180[g]	NA	-
Allegheny/Monongahela River (avg.)	625	373[g]	NA	-
Typical industrial (avg.)	625	42-435 (171)[h]	NA	-

[a] Unless otherwise stated, ranges were obtained from Reference 5, pp. 37-41. Averages shown in parenthesis are based on the data from questionnaire responses, Reference 5, p. 46. Maximum water use is assumed to be 625 ℓ/Mg of coke.

[b] Unpublished data received from E. Dulaney, U.S. EPA, March 20, 1980.

[c] Reference 6, pp. 42-45.

[d] Reference 7.

[e] Reference 8.

[f] Based on average of all plants, Reference 5, p. 46.

[g] Reference 9.

[h] Based on TDS levels in public water supply for 20 cities in which coke plants are located.

[i] Average of high and low values from pp. 37-41, Reference 5.

[j] Assume equal to pushing controls.

[k] Assumes 20% of total solids are emitted as particulate and 300 mg/ℓ total solids for natural water source.

NA - Data not available.

IMPACT OF BAFFLES ON QUENCH TOWER EMISSIONS

Historically, the method most frequently used to reduce particle and droplet emissions and subsequent fallout around the quench towers has been the installation of baffles (sometimes called mist eliminators) in the tower above the sprays. The baffles remove particulate and droplets from the emissions stream primarily by impaction. As described in References 3 and 4, a wide variety of baffle designs have been used in domestic quench towers to enhance this removal.

Few emissions data are available to directly evaluate the impact of such parameters as baffle configuration (e.g., number of rows, angle of baffles, spacing between baffles, and size of baffles) and the vertical location of the baffles in the tower on baffle performance. Because of this data gap, an engineering model has been used to estimate the performance of baffles.[2,10] The paragraphs below briefly describe the limited data, present the model that has been developed, and evaluate baffle performance based on that model.

No domestic test data which were obtained by isokinetic or near-isokinetic conditions and taken upstream and downstream of baffles or before and after baffle installation have been identified. The only such data that we have identified were obtained by Jackson and Waple[11] in Scotland in the late 1950's. In a series of tests using a suction sampling system and a 1-1/2 in. cyclone for collection, emission measurements were taken under five sets of baffle conditions: (a) no baffles; (b) wooden chevron baffles located in the top of the tower; (c) wooden chevron baffles located immediately above the sprays; (d) corrugated asbestos baffles near the top of the tower; and (e) corrugated asbestos baffles located immediately above the sprays. The results indicated that for the last three conditions the baffles were quite ineffective, providing only about 20% control. However, the chevron baffles installed in the top of the tower reduced particulate emissions by about 60%. While these results provide some insight to the performance of baffles, they should be viewed with some skepticism in that little is known about process parameters, specific test results, or the accuracy and precision of the sampling method.

In the absence of test data to definitively evaluate the performance of quench tower baffle systems, theoretical models that estimate performance have been examined. The model which we have chosen is described by Gorman, et al.,[3] and Ertel.[10] This model is based on the works of Calvert, et al.,[12,13] on zigzag baffle arrangements for mist eliminators in wet scrubbers. The choice of the model that represents zigzag baffles is appropriate in that almost all baffles currently employed in domestic quench towers are either zigzag baffle arrangements or are arrangements that can be approximated as a sequence of zigzag baffles.

Based on Calvert's model, the following expression for baffle efficiency as a function of baffle design characteristics and emission stream properties was developed:[3]

$$E = 1 - \exp \frac{- d_p^2 \rho_p U_g n\theta}{(515.7)\mu_g b\cos^2\theta} \qquad \text{Eq. 4}$$

where E = collection efficiency, fraction
d_p = particle diameter, cm
ρ_p = particle density, g/cm^3 (this value is assumed to be 1.4 since most particles are either coke or water)
U_g = superficial gas velocity, cm/sec
n = number of rows of baffles
θ = angle of baffle to flow path, degrees
μ_g = gas viscosity, poise (assumed to be 2 x 10^4)
b = horizontal spacing between two consecutive baffles in same row, cm

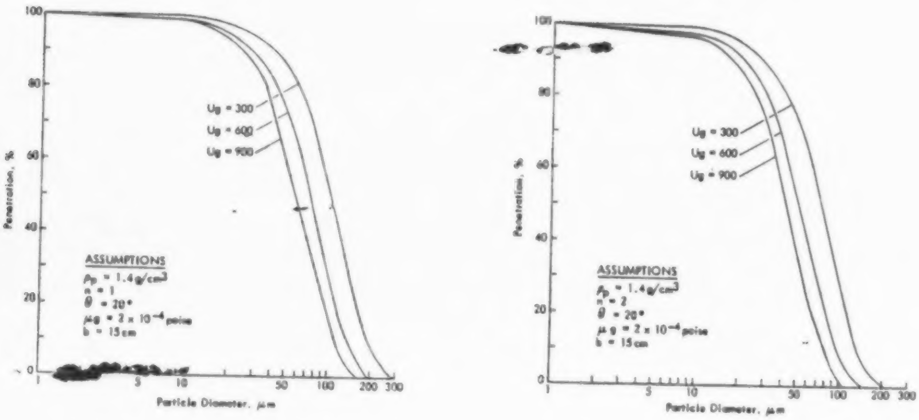
Note that the design parameters influencing baffle efficiency are the number of rows (or bends) in the system, the angle of each row or bend with respect to direction of gas flow, and the horizontal spacing between two baffles on the same row.

Although no quench tower data are available to compare measured efficiency with the estimated efficiency predicted by Equation 4, Calvert found that the theoretical collection efficiency compared well with the measured efficiency on tests of water droplet removal by a zigzag baffle mist eliminator. Further, these measured efficiencies were not greatly altered by entrained particulate in the water droplets. Both the physical characteristics of the quench tower emissions stream and available test data suggest that most particulate emissions are entrained in water droplets. Hence, Calvert's zigzag baffle model provides a reasonable model for quench tower baffle performance.

As shown in Figure 4, Equation 4 was used to develop performance curves for various baffle arrangements. These curves are plots of baffle penetration (one minus efficiency) versus particle (or droplet) size for three velocities which span the range of typical quench tower operating conditions. These curves show the dependency of performance on both particle size and gas velocity. They indicate that most arrangements are not very effective for particles (or droplets) less than 10 μm in diameter and are highly efficient for particles greater than 150 μm in diameter. Hence, the particle sizes of greatest concern when comparing different baffle arrangements are in the 10- to 150-μm range.

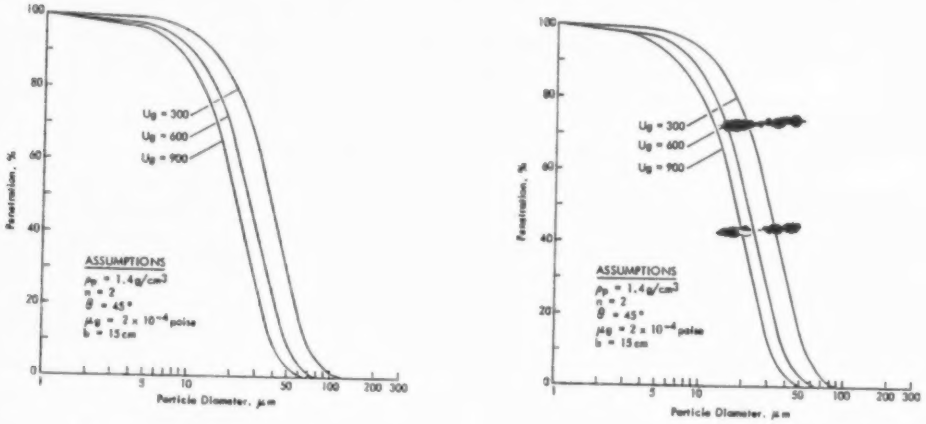
CONTROL SCHEMES AND THEIR IMPACTS

For any individual quench tower a range of controls is available, including control of quench water solids concentrations over a continuum of about 300 to 12,000 mg/ℓ and a variety of specific baffle configurations.



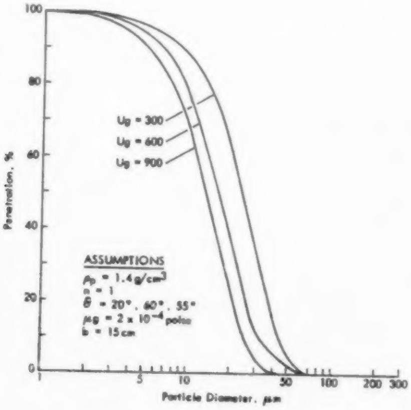
(a) Single row, 20°

(b) Double row, 20°



(c) Double row, 45°

(d) Triple row, 45°



(e) Carl Still

Figure 4. Performance curves for various baffle designs.

For our analysis of the impacts of water quality and baffle design control measures, we have chosen six control schemes which represent the range of available controls. These six control schemes are defined in Table 2.

The definitions of these control schemes and the subsequent discussions of emissions and secondary impacts are based on our analysis of currently available data. These data are limited, particularly with respect to the impact of multiple row baffles on emissions. The U.S. EPA is currently conducting extensive tests at DOFASCO to address these limitations. The results of those tests may modify the analysis and the conclusions that are developed in the following sections.

EMISSION IMPACT

As indicated earlier, for towers with single row baffles, the test data suggest a linear relationship between particulate emissions and the concentration of total solids in the quench water. Using Equation 3 and the best estimate of solids concentration from Table 2, average particulate emission factors for the first three control schemes are estimated to be:

TABLE 2. QUENCH TOWER CONTROL SCHEMES

Control Scheme	Water Control	Total Solids Concentration (mg/ℓ) Range	Total Solids Concentration (mg/ℓ) Current "Best" Estimate	Baffle Type
1	No Control	5,000 - 10,000	5,500	Single Row
2	Eliminate excess ammonia liquor and scrubber blowdown	1,000 - 2,000	1,800	Single Row
3	Local surface or ground water or equivalent	200 - 600	500	Single Row
4	No Control	5,000 - 10,000	5,500	Multiple Row[a]
5	Eliminate excess ammonia liquor and scrubber blowdown	1,000 - 2,000	1,800	Multiple Row
6	Local surface or ground water or equivalent	200 - 600	500	Multiple Row

[a] Multiple row baffles are those which are "most efficient" as defined by Equation 4. Our data include a double row of 20° baffles (DOFASCO), a double row of 45° baffles (Donner Hanna), a triple row of 45° baffles (Armco-Houston), and Carl Still baffles (U.S. Steel-Gary, Tower No. 3).

Control Scheme 1	1.2 kg/Mg
Control Scheme 2	0.69 kg/Mg
Control Scheme 3	0.50 kg/Mg

Hence, Control Scheme 2 results in an average emissions reduction of 42% and Control Scheme 3 a reduction of 58% from Control Scheme 1.

The data presented earlier also suggest that no relationship may exist between emissions and quench water total solids concentration for towers having multiple row baffles and solids concentrations of less than 2,000 mg/liter. This fact is suggested by the emissions data shown in Figure 5. Since no such relationship could be found, emissions for Control Schemes 5 and 6 are estimated to be 0.25 kg/Mg, the average of the five tests shown in Figure 5. This represents a 79% reduction from Control Scheme 1.

No test data are available to estimate the emissions rate for Control Scheme 4. Hence, the emissions rate for Control Scheme 1, the particle size data from tests at U.S. Steel-Lorain,[14] and Equation 4 were used to estimate emission rates for Control Scheme 4.

For Control Scheme 1, the particle size data from Lorain are used to divide the emissions into two size ranges, those less than 10 μm and those greater than 10 μm in diameter. This split results in the following size distribution:

	Emission Factor (kg/Mg)		
	< 10 μm	> 10 μm	Total
Control Scheme 1	0.70	0.50	1.2

To calculate the emissions levels, it was assumed that for the particulate less than 10 μm in diameter, single row baffles had no control, while multiple row baffles had about 10 to 25% efficiency. These values were based on the efficiency curves shown in Figure 4. Data were insufficient to determine particle size distribution of the particles >10 μm in diameter. Since Equation 4 is highly sensitive to size differences over this range, a sensitivity analysis was performed using estimates of mean particle size of 20 and 150 μm for the particles greater than 10 μm. Given the amount of fairly large droplets containing particulate in the quench tower emissions stream, 20 μm appears to be a reasonable minimum for the mean size for the +10 μm particles. The maximum mean size of 150 μm was calculated by Laube, et al.,[14] as the largest mean size that can be expected based on settling of larger droplets. The results obtained from applying equations to the data above are:

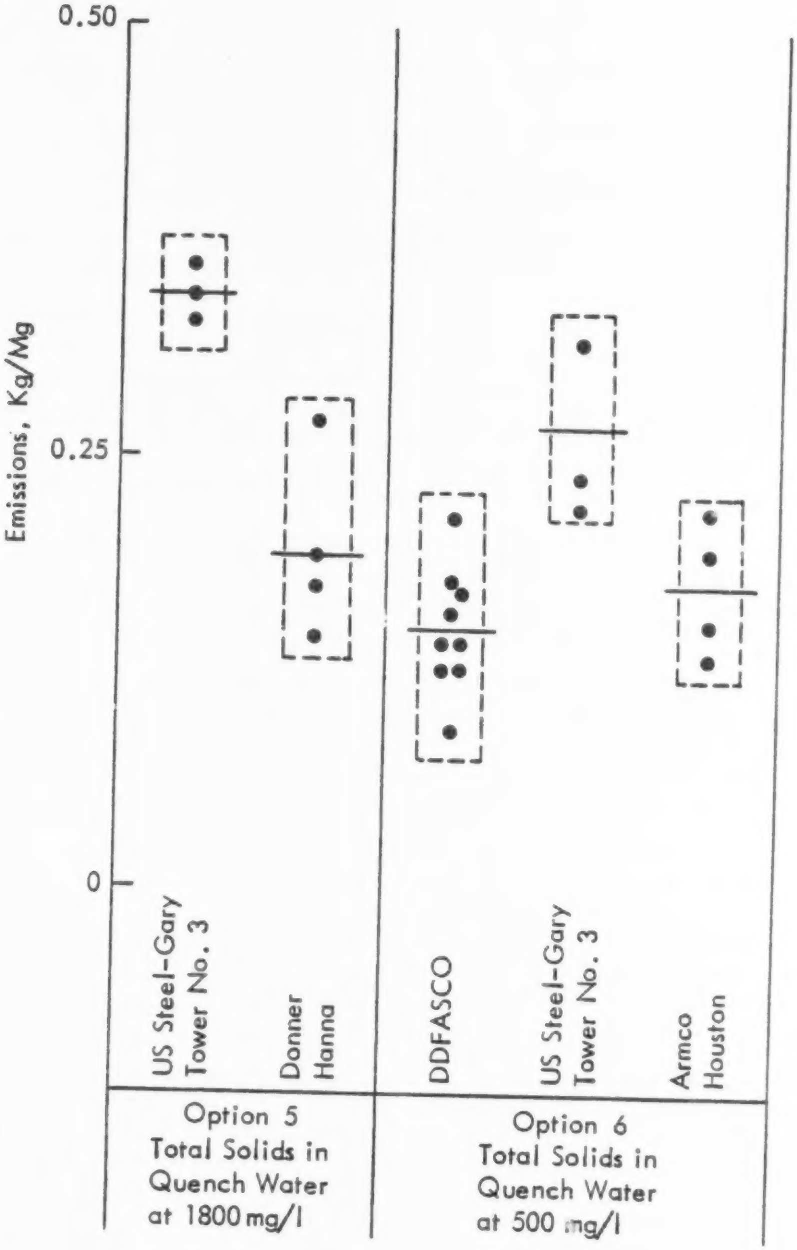


Figure 5. Emission data for control Schemes 5 and 6 (multiple row baffles).

	Emission Factor (kg/Mg)		
	< 10 μm	> 10 μm	Total
Control Scheme 4	0.52 - 0.63	< 0.0001 - 0.28	0.52 - 0.91

These data suggest a particulate reduction of 24 to 57% for Option 4 over Control Scheme 1.

In order to validate the conclusions, the same analysis was performed for Control Schemes 5 and 6 using the emissions estimates for Control Schemes 2 and 3 and assumptions on particle size from the U.S. Steel-Lorain data. We found that the model predicted emissions of 0.38 to 0.56 kg/Mg for Control Scheme 5 and 0.32 to 0.43 kg/Mg for Control Scheme 6.

While the above analyses provide an indication of the performance of multiple row baffles, the results should be viewed with some skepticism in that: (a) no test data are available on the accuracy of Calvert's model in predicting quench tower baffle performance; and (b) the available particle size data are quite limited. We anticipate that the results from the current DOFASCO tests will provide added data on baffle performance and particle size. These data should enable a more certain evaluation of performance for Control Scheme 4.

SECONDARY IMPACTS

Each of the control schemes described above has costs and secondary environmental impacts. These impacts influence the choice of control for a particular tower. The magnitude of the impacts is an important factor in the need for more knowledge of the performance of Control Scheme 4.

The use of multiple row rather than single row baffles has minimal cost and no secondary environmental impacts. Data from quench tower manufacturers indicate that the installation of multiple row baffles will increase the capital and annualized cost of baffling about 40%. There are no secondary environmental impacts since the particulate captured by the baffles is returned to the sump and eventually settles out as sludge. The sludge, which primarily is comprised of coke breeze, is periodically removed from the sump and is used in the coke oven or as a fuel for sintering.

On the other hand, the control of quench water quality may have significant cost and secondary environmental impacts. These impacts are related to the disposal of wastewaters that are excluded from use in the quench tower. Before these waters can be discharged, they must be treated to meet BAT (Best Available Technology Economically Achievable) or pretreatment standards. The capital cost of equipment necessary to treat the effluent is quite high. The annualized cost of treatment of water replaced in the quench tower is estimated to be in the range of 75 to 200% of the annualized cost of a new quench tower (depending upon the quantity of water which must be treated).

In addition to the cost impact, the control of water also has secondary environmental impacts. Any coke plant wastewaters not used in the quench water are added to the plant effluent. These waters will be treated to meet BAT standards. While this treatment will remove most of the organic constituents, oil and grease, and suspended solids from the water, it will not affect the dissolved solids, primarily chloride salts. These salts may adversely affect surface waters near these plants.

Treatment of the wastewater will also produce a sludge which must be disposed of. These sludges will include biological sludge and lime or caustic soda from treatment of excess ammonia liquor in lime stills. Because of their chemical composition, the lime still sludges have been classified as a hazardous waste, increasing disposal problems for the waste sludges.

CONCLUSIONS

1. For towers with single row baffles, particulate emissions are linearly related to the solids concentration in the quench water over the range of solids concentrations found in domestic quench towers.
2. No relationship is found between particulate emissions and solids concentrations in the range of 300 to 2,000 mg/ℓ for quench towers with multiple row baffles.
3. More emission test data are needed to define the performance of multiple row baffles when used in quench towers.
4. Because of the large cost and secondary environmental impacts associated with the control of quench water solids, knowledge of multiple row baffle performance under high solids conditions is essential.

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CURRENT REGULATIONS AND CONTROL PERFORMANCE FOR VISIBLE EMISSIONS FROM WET-COAL CHARGING, DOOR LEAKS, AND TOPSIDE LEAKS

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ABSTRACT

The Research Triangle Institute, under contract to the U.S. Environmental Protection Agency (EPA), compiled background information on emissions from wet-coal charging, door leaks, and topside leaks from coke ovens. The study was undertaken as part of EPA's effort to examine the need for coke oven regulations. This paper summarizes a portion of the background information which was compiled. Current regulations from State Implementation Plans, consent decrees, and Occupational Health and Safety Administration (OSHA) requirements are summarized. Emission test results and performance data in terms of visible emission control are presented.

1.0 INTRODUCTION

Nearly all of the metallurgical and foundry coke produced in the United States is produced in slot-type, by-product recovery coke ovens. There are approximately 13,000 such ovens located in 199 batteries at 58 plants. Ninety-three percent of coke-making capacity is owned by integrated steel companies and the remainder is owned by independent merchant coke producers. Coke oven batteries are located in 17 states, with 55 percent of the capacity in Pennsylvania, Ohio, and Indiana.

The emission points that were examined include the wet-coal charging operation, door leaks, and topside leaks. In a wet-coal charging system, gases and particulate can be emitted from the oven charging ports throughout the 3 to 8 minute charging period. Charging emissions may be visible at the point where the charging car drop sleeves meet the charging ports, or from the top of the charging car if emissions have escaped up through the drop sleeves and coal hopper. During the coking period (usually 16 hours or more), emissions may leak from the doors, charge port lids, and offtake piping system on the oven. In addition, leaks occasionally occur in the collecting main(s) which carries the off-gases to the by-product recovery plant.

Since 1975, methods have been developed by EPA and State agencies to measure visible emissions from coke oven charging, door leaks, and topside leaks. The method for charging most widely used involves reading not opacity, but cumulative seconds of visible emissions during the charging period. When coal begins flowing from a charging car hopper into the oven, the observer starts recording on an accumulative stopwatch the time during which he sees any visible emissions from the charge ports, or from the tops of the charging car hoppers. The stopwatch may be started and stopped several times during a charge. The observation ends when the last charge port lid is replaced. After several consecutive charges are observed, a sum or average of the number of seconds of visible emissions associated with charging is determined.

Visible emissions from door leaks are measured by a walk around the battery with the observer pausing at each oven to observe leakage from the doors and door areas out to the buckstays. Any visible emission qualifies the door as leaking. When machinery blocks the observer's view of a door, he may return later as long as the total time to read all doors does not exceed 45 minutes. The percent of the total number of doors on operating ovens that are leaking is then determined and the result is recorded as "percent leaking doors" or "PLD."

Topside leaks are measured in the same way. Leaks from charge ports and offtake systems are recorded separately and a "percent leaking" value is determined for each. The abbreviations are PLL for percent leaking lids (i.e., charge port lids) and PLO for percent leaking offtakes.

2.0 CURRENT CONTROL REQUIREMENTS

Coke oven batteries are currently subject to the control requirements of State implementation plans (SIP's) and Occupational Safety and Health Administration (OSHA) standards. In addition, some batteries must meet the requirements of consent decrees that have been negotiated on a plant-by-plant basis. SIP's and consent decrees contain emission limits for charging, door leaks, and topside leaks. The OSHA standards regulate worker exposure and specify certain required engineering and work practice controls.

Table 1 presents a summary of current SIP emission limits. These SIP limits are at different stages of the federal approval process. Charging limits range from 60 seconds as a sum of 4 consecutive charges to 170 seconds for 5 charges. Door leaks range from 10 to 16 PLD, charge port lids from 2 to 5 PLL, and offtake systems from 5 to 10 PLO. Measurement methods vary somewhat, but most are very similar to what have been described above. EPA has issued Reasonably Available Control Technology (RACT) guidance for iron and steel particulate emission sources including coke ovens (45 FR 59198). That guidance calls for 25 seconds per charge averaged over 4 to 7 charges (with an optional exclusion of the highest reading in 20 observations), 10 PLD, 5 PLL, and 10 PLO. Based on current regulations, 68 to 100 percent of coking capacity would be at the RACT guidance level or below. A summary of current regulations and the number of affected batteries is given in Table 2. The effect of excluding one charge in 20 observations has not been considered in this analysis.

TABLE 1. STATE REGULATIONS FOR COKE OVEN EMISSIONS

State	Charging (seconds per charge)	Percent maximum leaking		
		Doors	Lids	Offtakes
Alabama	a	15	5	10
California	60/4	10	3	10
Illinois	170/5[b]	10	5	10
Indiana	125/5[c]	10[d]	3	10
Maryland	160/5	10	3	10
Michigan	80/4	10-12[e,f]	4	4
Missouri	120/6	15	2	10
New York	150/5[c]	10[f]	2	5
Ohio	170/5	16	5	10
Pennsylvania	75/4	10[g]	2	5
Wisconsin	h	10	5	10

[a] Visible emissions $\leq$ 20 percent opacity except for $\leq$ 3 min/hr.
[b] 200/5 for existing 5-meter, 3-hole batteries.
[c] May exclude one in 20 charging observations.
[d] Excludes four doors.
[e] Ten percent for short batteries and 12 percent for tall batteries.
[f] Chuck doors are counted as separate doors.
[g] Excludes two doors, counts all door area leaks.
[h] Equipment and work practice requirements.

Consent decrees have been signed for batteries representing about one-third of coke-making capacity. These decrees were generally negotiated as settlements of outstanding SIP violations and may specify required equipment and work practices as well as visible emission limits. All but a few consent decree limits are equal to or more stringent than the RACT guidance level. The lowest emission limits currently in effect apply to new or rebuilt batteries. Several consent decrees for these new batteries have limits of 55 seconds for 5 charges, 5 PLD, 2 PLL, and 5 PLO.

In 1976, OSHA promulgated standards designed to protect workers from exposure to coke oven emissions. One part of the rule sets a limit on worker exposure which is to be monitored quarterly by the company and during OSHA inspections by OSHA personnel. Another part specifies engineering and work practice controls and includes general prohibitions on fugitive emissions. Because specific visible emission limits are not given in the rule, direct comparison of OSHA requirements with SIP and consent decree limits is not possible.

TABLE 2. SUMMARY OF BASELINE CONTROL REQUIREMENTS

	Number of batteries	Percent of capacity
	CHARGING	
Charging limit (avg s/chg)		
No limit	23	7.4
30-40	44	24.7
25	32	21.7
19-20	62	33.4
15	7	2.9
11-12	15	10.0
	DOOR LEAKS	
Percent leaking doors		
20	1	0.5
15-16	51	21.5
~12	76	48.2
10	46	24.4
8	3	1.7
4-5	6	3.7
	LID LEAKS	
Percent leaking lids		
5	58	26.4
4	9	7.3
3	40	21.8
2	71	41.7
1	5	2.7
	OFFTAKE LEAKS	
Percent leaking offtakes		
15	1	0.5
10	109	55.4
6	3	1.7
5	56	32.3
4	14	10.0

3.0 EMISSION ESTIMATES

Coke oven emissions consist of a yellow-brown gas which contains over 10,000 compounds as gases, condensible vapors, and particulates. The components of primary concern include the known or suspected carcinogens belonging to a class of compounds termed polycyclic organic matter (POM). POM, which condenses on fine particulates at ambient temperatures, consists of compounds with two or more fused rings. There are thousands of POM compounds which vary widely in physical and chemical characteristics. These pollutants are sometimes reported as benzene soluble organics (BSO) or as a quantity of a specific surrogate compound, such as benzo(a)pyrene (BaP). BSO is composed of many compounds, some of which are not POM.

The emission of pollutants is generally characterized by both the concentration and the flow rate of the pollutant stream. However, these characteristics are difficult to apply to emissions from coke oven doors, lids, offtakes, and charging. The rates of emissions are highly dependent on the time into the coking cycle, the gap size, the number of gaps, and oven pressure. The concentration of pollutants also varies with time, and there may be a variation in the concentration of BSO from battery to battery caused by operating conditions and the coal type or blending practices. Even if the leaks were well characterized in terms of the size and length of the gap, there would be potential difficulties in assessing the flow rate of the pollutant. Measurement of the concentration of the BSO above the coke battery is difficult because the concentrations are transient. The monitored particulate concentration is a function of the location of the sampler, the existing wind conditions, and interference from other emissions.

The collection and measurement of fugitive coke oven emissions is further complicated by the fact that the gases which are emitted from the oven condense on metal surfaces present in the sampling system. These tars even condense on the hot oven jambs. This condensation can lead to erroneous results when the gases are carried through ducts before they reach the sampling device.

3.1 CHARGING EMISSIONS

Particles emitted during the charging cycle have been identified as coke balls, pyrolitic carbon, high-temperature coke, char, coal, mineral matter, and fly ash.[1 2] For this type of fugitive emissions source, collection of representative emission samples is extremely difficult and, consequently, very little data on mass rates are available. Estimated emission factors in the literature vary by at least one order of magnitude, and the accuracy of the emission factor should be judged according to this variation. The following emission estimates are given in terms of g BSO/kg coal and g particulate/kg coal.

With the assistance of the American Iron and Steel Institute, EPA has compiled and analyzed data on particulate emissions from iron and steel mills to assist in the definition of particulate emission factors for each process. This study suggests an emission factor for uncontrolled charging of .25 to .75 grams of particulate per kilogram (0.5 to 1.5 lb/ton) of coal charged.[3] This range is based on measurements of particulate deposition on greased plates and from the solids collected from tests of a scrubber to control charging emissions. The mid-range value yields an estimate of about 0.5 g particulate/ kg coal.

In addition to the AISI estimate, a test was conducted by EPA at J&L Steel, Pittsburgh, to compare the American Iron and Steel Institute (AISI) larry car with a conventional Wilputte larry car.[4] Samples were collected by putting enclosures around the Wilputte larry car drop sleeves and evacuating the emissions through a stack where they could be sampled. Isokinetic conditions could not be maintained because of a high variability in the flow of emissions. The reported particulate measurements represented composite samples from different emission points. The particulate catch averaged 815 g/charge, or about 0.05 gram of particulate per kilogram of coal (0.1 lb/ton) from tests of 10 charges with an average sampling time of 3.5 min. The average amount of BSO measured (excluding the impinger catch) was 57 percent. The impingers averaged 96 percent of the mass collected in the front of the sampling trains and contained an average of 60 percent BSO.[4] The particulate emission factors were combined with these results to calculate a BSO emission factor of 0.055 g BSO/Kg coal. The particulate emissions are based on particulate captured by the filter and do not reflect the BSO collected in the impingers. The resulting mass emission estimates for poorly-controlled charging is 0.05 to 0.5 g particulate/kg coal, or roughly 0.055 to 0.55 g BSO/kg coal.

Emissions from uncontrolled or poorly-controlled charges generally appear as dense clouds. In contrast, during observation of charges controlled by the stage charging operating procedure, EPA observers noticed that during good charges (a small duration of visible emissions), the emissions were generally small wisps or puffs which drifted from around the drop sleeves on the larry car. For charges where the duration was longer, the emissions changed to clouds of smoke which escaped to the atmosphere with higher velocities. Generally, the longer the duration, the more large clouds and fewer wisps were seen. A series of inspections were conducted in which one inspector recorded seconds of emissions greater than 20 percent opacity, and another inspector recorded seconds of any visible emissions. For charges with 25 seconds or greater of any visible emissions, there was very little difference in the two methods. For charges with less than 25 seconds of emissions, the difference in the two methods is significant. For example, the variance in the two methods is 21 percent for 15 seconds of emissions, and the variance increases to 47 percent for 5 seconds of emissions. These results imply that the concentration of pollutants is less for a short duration of visible emissions which are often composed of wisps with an opacity less than 20 percent.

3.2 DOOR LEAK EMISSIONS

The fugitive nature of door leaks has posed the same collection and sampling problems that were previously discussed. Probably the most reliable coke oven door data are those gathered on BSO emissions from cokeside sheds. A cokeside shed is a large hood which extends over the entire coke side of the battery to capture both pushing and cokeside door emissions. Available cokeside shed test results are generally representative of high levels of percent leaking doors (i.e., levels greater than 30 PLD). Emission factors for door leaks are given as g/kg coal and as an average rate for a leaking door.

In May 1977, EPA conducted four 10-hour tests of Wisconsin Steel's shed that covered the coke side of 45 5-meter ovens.[5] Sampling was discontinued during pushing so that the data would only reflect emissions from doors. BSO emissions (from the full sampling train) during the test averaged 6 kg/hr from an average of 31 leaking doors (70 PLD) with a resulting emission factor of about 0.25 g BSO/kg coal (or about 0.2 kg BSO/hr for a leaking door). Particulate emissions (front half) ranged from 0.17 to 0.21 g/kg coal, or 65 to 85 percent of the BSO.

A similar test was conducted at Armco, Inc. in Houston, Texas, in October 1979.[6] [7] The Armco shed encloses the coke side of 62 4-meter ovens. Three tests conducted during nonpush periods measured 6.8 to 13 kilograms of BSO per hour from 10 to 24 leaking doors (16 to 39 PLD).[6] The resulting emission rate is about 0.6 kg BSO/hr for a leaking door or 0.4 to 0.8 g BSO/kg coal.

Bethlehem Steel sampled emissions from its Burns Harbor shed on Battery 1.[5] The shed covers the coke side of 82 6-meter ovens. During these tests, BSO emissions during nonpush periods averaged 3.9 kg/hr; the number of doors leaking was not reported. Bethlehem Steel also sampled emissions from temporary stacks mounted on pusherside doors at their Burns Harbor plant. A total of 14 samples were collected at four doors that were completely enclosed between buckstays. Toluene soluble organics averaged 0.22 kg/hr for each door.

The shed test data, summarized in Table 3, reveal a range of BSO emissions of approximately 0.2 to 0.7 kilogram of BSO per hour per leaking door for the tests where the number of leaking doors was recorded. A range of 0.25 to 0.8 g BSO/kg coal was derived from these tests. Based on the Wisconsin Steel tests, particulate emissions (front half) are estimated as 0.16 to 0.68 g/kg coal.

TABLE 3. COKESIDE SHED TEST RESULTS

Test	Kilograms of BSO/hour	Number of leaking doors	PLD	Kilograms of BSO/ hour/leaking door
Wisconsin Steel Shed	7.0	33	73	0.21
	5.9	35	78	0.17
	5.4	27	60	0.20
	6.0	31	69	0.19
Average	6.1	32	70	0.19
ARMCO, Inc. Shed	6.8	10	16	0.68
	11	19	31	0.59
	13	24	39	0.55
Average	10.3	18	29	0.58

3.3 TOPSIDE EMISSIONS

An emission test was conducted at U.S. Steel's, Clairton Battery 1 by EPA in August 1978 to measure topside leak emissions.[8] During the second hour of coking, samples were collected from a vent pipe which had been installed on a charging port lid. The leak rate was adjusted to yield small leaks with a 0.3-meter (1-foot) visible plume and large leaks with a 1- to 2-meter (3- to 6-foot) visible plume. The results, listed in Table 4, show a range of 0.0017 to 0.0053 kg/hr for a small leak, with an average rate of 0.003 kg/hr. Emissions from the large leak ranged from 0.012 to 0.035 kg/hr, with an average rate of 0.021 kg/hr. The analysis for BaP showed that 1.4 to 1.8 percent of the BSO was BaP.

TABLE 4. TOPSIDE LEAK EMISSION TEST[8]

Leak size	BSO(kg/hr)
Large (1-2 m)	0.017
	0.035
	0.012
Average	0.021
Small (0.3 m)	0.0017
	0.0029
	0.0053
Average	0.0033

These emission rates can be used to derive an emission factor in g/kg of coal by assuming a typical battery on an 18 hour cycle time with 62 ovens, 3 lids and 2 offtakes per oven, and 16 Mg coal per oven. Also assume that current control performance is 3 PLL and 10 PLO which would yield 18 topside leaks. The emission factor for this case would be 0.001 g BSO/kg coal if all of the leaks are small, and 0.01 g BSO/kg coal if all of the leaks have large plumes. Particulate emissions were not measured during the topside leak test, but they are expected to be similar to door leak emissions (65 to 85 percent of the BSO).

4.0 CONTROL TECHNOLOGY AND PERFORMANCE

The current control techniques used by the industry were reviewed to identify equipment and procedures which have been demonstrated for control of charging, door leaks, and topside leak emissions. The performance data were collected by EPA personnel or their contractors during official EPA inspections.

4.1 CONTROLS FOR CHARGING

Current regulations require stage charging and the associated equipment modifications. Stage charging is a systematic procedure for introducing pulverized coal into a coke oven so that an open passage is constantly maintained for the exit of gases to the collecting main. This procedure allows gases and other matter that evolve during charging to be effectively contained within the oven while they are being drawn into the collecting main by steam aspiration and then exhausted through the regular gas handling equipment to the by-product recovery plant. Containment and removal of pollutant-laden gases occur with minimal losses to the atmosphere.

The requirements for good stage charging include:

- The stage charging operating procedure.
- Battery modifications, such as repaving the battery top or modifying the coal bunker on some batteries.
- New or modified larry cars with increased capacity in the outer hoppers, independently operated drop sleeves, and independent hopper control of coal flow.
- Double drafting with either a second collecting main or jumper pipe.
- Adequate steam aspiration.
- Control of coal bulk density.
- A smoke boot on the leveler bar.
- Gooseneck cleaning.
- Decarbonizing equipment.
- Training program for employees.

Battery top workers and the operating procedures they follow perform an equally important role in emission control. Detailed observation of charging practices revealed that even the best controlled batteries experienced occasional lapses in work practices or equipment malfunctions which resulted in higher emission levels. A few of the worker job functions that are critical to control of emissions from charging include inspection and cleaning of goosenecks, prompt lid replacement, turning the aspiration system on and off, observing the position of drop sleeves, and spotting the larry car.

4.2 PERFORMANCE DATA

The U.S. Steel Clairton Works has developed a stage charging system. In addition to the physical ability to stage charge, emission control was optimized through extensive training, observation, and monitoring programs. Topside manpower was increased by creating a utilityman position with the prime responsibility of providing assistance to the larry car operator for gooseneck cleaning and other environmental responsibilities. Process observers were also employed to monitor emission performance and to identify when corrective action might be needed. Supervisory personnel are informed of equipment problems and deviations from prescribed work and operating practices.[9]

CF&I also reported a program to optimize control of charging emissions. The company studied the charging procedure and established priorities for improving equipment and work practices which caused the greatest amount of emissions. Equipment modifications were made and detailed operating and inspection procedures were developed. The company also reported that inspections and recordkeeping are important to identify the cause of control problems so that the trouble area or condition could be eliminated. The recordkeeping also monitors progress, obtains operator involvement, reinforces productive efforts, directs maintenance efforts, and documents improvements.[10]

Visible emission data on the CF&I and U.S. Steel Clairton charging operation were compiled and analyzed. These data included observations from 92 charges at CF&I and 16 to 65 charges per battery at Clairton. A statistical analysis of the charging data was performed to obtain confidence intervals that described individual battery performance. The data were not characterized by a normal distribution. To allow the application of normal statistics, various data transformation techniques were investigated to determine an appropriate transformation that would yield a normal distribution. A transformation of log (S + 1), where S is equal to seconds of visible emissions, provided a normal distribution for independent groups of five or more consecutive observations.

The variance components used in calculating the confidence levels include the variance between observers within charges, between charges within days, and between days. Based on 10 observations and the variance components, the 15 batteries listed in Table 5 had log averages of 0.5 to 11 seconds per charge with a range of 95-percent confidence levels of 1 to 16 seconds per charge. The lowest levels of visible emissions were observed on Batteries 16 and 17 which were using run-of-the-mine coal. The highest level was a log average of 11 seconds per charge with a 95-percent confidence level of 16 seconds per charge.

TABLE 5. DATA FOR OPTIMIZED STAGE CHARGING[a]

Company	Battery	Arithmetic average	Log average[b]	95-percent level
U.S. Steel, Clairton	16	1.0	0.5	1.2
	17	1.2	0.8	1.7
CF&I, Pueblo	B	5.4	4.5	7.4
U.S. Steel, Clairton	1	8.6	4.8	7.9
	22	6.6	5.1	8.3
	10	8.8	6.0	9.8
	19	6.8	6.1	9.9
	3	7.8	6.9	11.2
	7	7.6	7.3	11.6
	21	13.1	7.3	11.7
	9	8.4	7.5	12.0
	2	9.0	7.7	12.4
	8	8.9	8.1	13.0
	20	12.0	8.1	13.0
	11	11.6	11.1	16.1

[a] All results are seconds of emissions per charge.

[b] Log average = $e^{Y}-1$, where $Y = (\ln(s_1 + 1) + \ln(s_2 + 1) + \ldots \ln(s_{10} + 1))/10$

TABLE 6. ADDITIONAL STAGE CHARGING DATA

Company	Battery	Arithmetic average	Log average	95-percent level
U.S. Steel, Fairfield	9	5.4	4.0	6.7
	6	10.0	6.8	10.9
Shenango, Neville Island	3	6.1	5.1	8.4
	4	6.6	6.2	10.0
J&L, Pittsburgh	P2	7.3	5.6	9.1
	P4	6.2	5.6	9.1
Lone Star Steel	C	7.4	6.6	12.0
U.S. Steel, Gary	1	13.0	8.4	15.0

Other batteries which used the stage charging procedure were also examined, and although these plants have not reported the extensive optimization of Clairton and CF&I, the control performance is similar. The data in Table 6 represent a range of battery types, including single and double collecting mains, short and tall batteries, different battery ages, variety of coal sources, and a variety of equipment and construction features.

4.3 DOOR LEAK CONTROLS

Most batteries control door leaks with doors and seals that are called "self-sealing." This means that the small gaps between the metal seal and door jamb are sealed by the condensation of tar from the coke oven gas.

Current regulatory requirements include replacement of damaged doors, seals, and jambs for some batteries and a basic door leak control program for all batteries. The door leaks control program involves:

- Routine inspection and cleaning.
- Proper door placement and seal adjustment.
- Maintaining door seals within specifications ("blueprinting").
- Prompt replacement or repair of damaged doors, seals, and jambs.
- Improvements to the door repair shop.

Metal seals are most effective when they are new, properly adjusted, and used on relatively clean, straight jambs. Effective sealing can be inhibited by several factors such as distortion and damage to jambs, doors, sealing strips, and adjusting hardware. Most of the components of the oven's doors assembly are tightly constrained; consequently, when the assembly is heated, gross distortions are prevented. Thermal cycling under these constrained conditions causes thermal warping and damage to the metal components. Inspection, maintenance, repair or replacement, blueprinting, and better materials of construction are the elements that would be necessary to overcome these causes of door leaks. The basic door leak control program also includes cleaning and adjustment. Cleaning removes encrustations which can cause gaps between the sealing edge and jamb. Proper door placement and adjustment of the seal in place are also important aspects of effective door leak control.

The batteries at CF&I and U.S. Steel, Clairton have been equipped with modified door seals and springs constructed with more temperature resistant, durable alloys. The modified seals, coupled with the basic door leak control program, have provided consistent control of door leak emissions.

4.4 DOOR LEAK PERFORMANCE

The modified seal technology coupled with a leak control program of routine inspection, cleaning, and repair has been implemented on the batteries at CF&I in Pueblo, Colorado, and U.S. Steel in Clairton, Pennsylvania. Other batteries have demonstrated a control performance that is equivalent to the performance of the CF&I and U.S. Steel, Clairton batteries without implementing the modified seal technology. However, the technology for door leak control has been defined to explain one method that has been used by the industry to achieve effective emission control. The 19 battteries in the data base are listed in Table 7 and include a range of battery types with original construction dates that range from 1951 to newly rebuilt.

TABLE 7. SUMMARY OF DOOR LEAK DATA

Company	Battery	Average PLD	Range PLD
U.S. Steel, Clairton	3	0.6	0 - 1.6
	1	0.9	0 - 2.3
	2	2.2	0 - 5.5
	7	2.9	0 - 5.5
	21	3.0	1 - 5.7
	22	3.4	2.3 - 5.2
	19	3.9	3.4 - 4.6
	20	4.5	2.3 - 7.5
	16	5.0	4.2 - 6.7
	10	5.8	4.8 - 7.1
	8	6.1	5.5 - 6.3
	17	6.2	4.9 - 8.2
	11	8.6	4.7 - 14.1
	9	9.0	3.9 - 16.4
CF&I	C	3.2	1.1 - 6.4
	B	4.3	0.8 - 9.2
	D	5.9	1.1 - 16.1
U.S. Steel, Fairfield	9	3.9	2.7 - 4.8
	2	7.2	3.0 - 13.0

The door leak data were characterized by a Poisson distribution. Analysis of the data revealed that 12 of the batteries averaged less than 5 PLD, and all 19 averaged less than 9 PLD. The 95-percent confidence level of the highest average, 9 PLD for Battery 9 at U.S. Steel, Clairton, is 12 PLD for an average of three inspections.

4.5 TOPSIDE LEAK CONTROL

Topside leaks occur around the rim of charging port and standpipe lids; standpipes can also leak at thier bases or through other cracks. These leaks are primarily controlled by proper maintenance and operating procedures which include:

- Replacement of warped lids,
- Cleaning carbon deposits or other obstructions from the mating surfaces of lids or their seals,
- Patching or replacing cracked standpipes,
- Sealing lids after a charge or whenever necessary with a slurry mixture of clay, coal, and other materials (commonly called lute), and
- Sealing cracks at the base of a standpipe with the same slurry mixture.

Because there are many places where leaks can develop, keeping all charging lid and standpipe leaks sealed is a continuous job. In essence, success in controlling these emissions is directly related to the amount of manpower, dedication of the employees, and the priorities of management.

Some equipment designs may reduce the effort required to keep leaks sealed. Heavier lids or better sealing edges may reduce leaks. Automatic lid lifters can rotate charging-hole lids after they are seated and provide a better seal. Even with such equipment, manual effort will still be required to seal leaks.

4.6 TOPSIDE LEAK CONTROL PERFORMANCE

The technology for controlling lid and offtake leaks is luting manpower, improved luting mixtures, modification or replacement of offtakes on some batteries, and the conscientious sealing (luting) of leaks when they are observed. This technology has been implemented on the batteries at U.S. Steel, Clairton. The conscientious luting of leaks was observed during EPA inspections of these batteries.

The topside leak data base is large and is not reproduced here because of space limitations. The 23 batteries in the lid leak data base include all of the U.S. Steel batteries at Clairton. Fourteen batteries averaged 0.2 PLL or less during at least one inspection, and the highest average of all 23 batteries was 1.8 PLL. The 95-percent confidence level associated with this average is 3 PLL when averaged over three runs. In the offtake leak data base, 11 batteries at U.S. Steel, Clairton averaged 0.7 to 3.4 PLO. The 95-percent confidence level associated with the average of 3.4 PLO is 6 PLO when averaged over three runs.

These levels of control performance have been achieved through proper equipment design and maintenance and through consistent application of luting materials to seal leaks. For many batteries, attaining these levels of control may require the addition of one worker to the topside area. In addition, it may be necessary to repair, modify, or replace damaged or poorly designed offtakes on some batteries.

5.0 SUMMARY

Current regulations for visible emissions from wet-coal charging, door leaks, and topside leaks range from 11 to 40 seconds per charge, 4 to 16 PLD, 1 to 5 PLL, and 4 to 10 PLO. More than 50 percent of the batteries have current emission limits that are less than or equal to 25 seconds per charge, 12 PLD, 3 PLL, and 10 PLO. The batteries at U.S. Steel's Clairton Works and at CF&I have optimized the stage charging procedure. Inspections at these plants showed varying control performance which ranged from a log average of 0.5 to 11 seconds per charge with a 95-percent confidence level of 1 to 16 seconds per charge. Several other batteries have demonstrated a control performance within this range. The average control performance for door and topside leaks at U.S. Steel's Clairton Works ranged up to 9 PLD, 1.8 PLL, and 3.4 PLO. The 95-percent confidence levels associated with these averages are 12 PLD, 3 PLL, and 6 PLO when averaged over three runs.

6.0 ACKNOWLEDGMENTS

This paper represents a portion of the information gathered under contract to EPA's Office of Air Quality Planning and Standards (OAQPS). The authors wish to acknowledge the cooperative effort and contributions of many individuals within OAQPS, EPA's regional offices, State agencies, the American Iron and Steel Institute, and the American Coke and Coal Chemicals Institute. These individuals provided guidance, data, and review of the background information on coke oven emissions.

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A REVIEW OF SHED AND GAS CLEANING SYSTEMS FOR CONTROLLING COKE PUSHING EMISSIONS FROM COKE PLANTS

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ABSTRACT

The body of information in this paper is directed to coke producers and their management, the environmental control agencies, and labor organizations interested in further protection of their members.

There are a number of different areas of concern in pollution control for coke ovens. We are directing our efforts to properly control all the emissions on the coke side of the oven.

In the United States in the past seven to ten years, there have been a number of concepts used by the steel industry and coke producers to control pushing emissions and door leakage on coke side of ovens. These concepts included various types of quench cars, land based systems, hooded hot cars, and sheds.

The purpose of this paper is to review the evolution of the shed concept up to the present and the new concepts presently being offered. We will also review and compare the gas cleaning devices used on the early sheds which were either high energy scrubbers or wet electrostatic precipitators versus the baghouse which is today's accepted technology on coke pushing emissions.

INTRODUCTION

A coke side shed is a special designed structure that is erected on the coke delivery side of a battery of coke ovens. Its purpose is to capture all the emissions developed on that side of the ovens from the following sources:

1. Removal of doors
2. Actual pushing
3. Spillage
4. Door leakage

The coke side shed properly designed and installed can control all of these sources.

Once of the first sheds was developed and installed by the Great Lakes Carbon Corporation at their St. Louis, Missouri, coke plant in the early 1970's. Figure 1 shows a cross section of this concept which was patented by the Great Lakes Carbon Corporation under U. S. Patent 3,844,901. This type shed was installed at four (4) steel companies in the United States and Canada in the middle 1970's and have been reasonably successful. This type shed is presently being installed on eleven (11) ovens at four (4) locations at other steel mills in the United States. The shed is a totally passive system with no moving parts. One it is installed and working, it is just there.

On the first sheds installed in the early to middle 1970's, the gas cleaning devices that were installed on the Great Lakes Carbon type sheds were flat plate continuously flushed electrostatic precipitators. The reasons for using the wet precipitator as the gas cleaning device were as follows:

1. Both the particulate and the condensable hydrocarbons were required to be collected. The condensables could only be collected by a wet device. The gaseous hydrocarbons that could condense at low temperatures in an EPA train would pass right through a dry baghouse.

2. There was concern by both the steel and coke producing industries and the baghouse manufacturers that the hydrocarbons could cause plugging of the fabric resulting in extremely short bag life or inability to meet the guarantees.

3. The pilot testing of the wet precipitator showed it could achieve extremely low levels of outlet grain loading or high efficiency when both the front half and back half were considered. Outlet loadings as low as .003 grs/SCF were achieved with inlet loadings as low as .03 grs/SCF giving an overall efficiency of 90%. These outlet loadings were also achieved during the pushing operations. In tests at four (4) coke plants at steel companies in the United States and Canada, these efficiencies could be achieved with the wet electrostatic precipitator.

Like any pollution control system installed in a large process plant, the combination MikroPul shed and wet precipitator had advantages and disadvantages. Some of the main pluses for the system were:

1. A totally passive system -- no moving parts.

2. Workers under the shed not exposed to elements.

3. Workers not exposed to any increase in coal tar pitch volatile levels.

4. Door leakage positively controlled.

5. All pollution sources under the shed controlled.

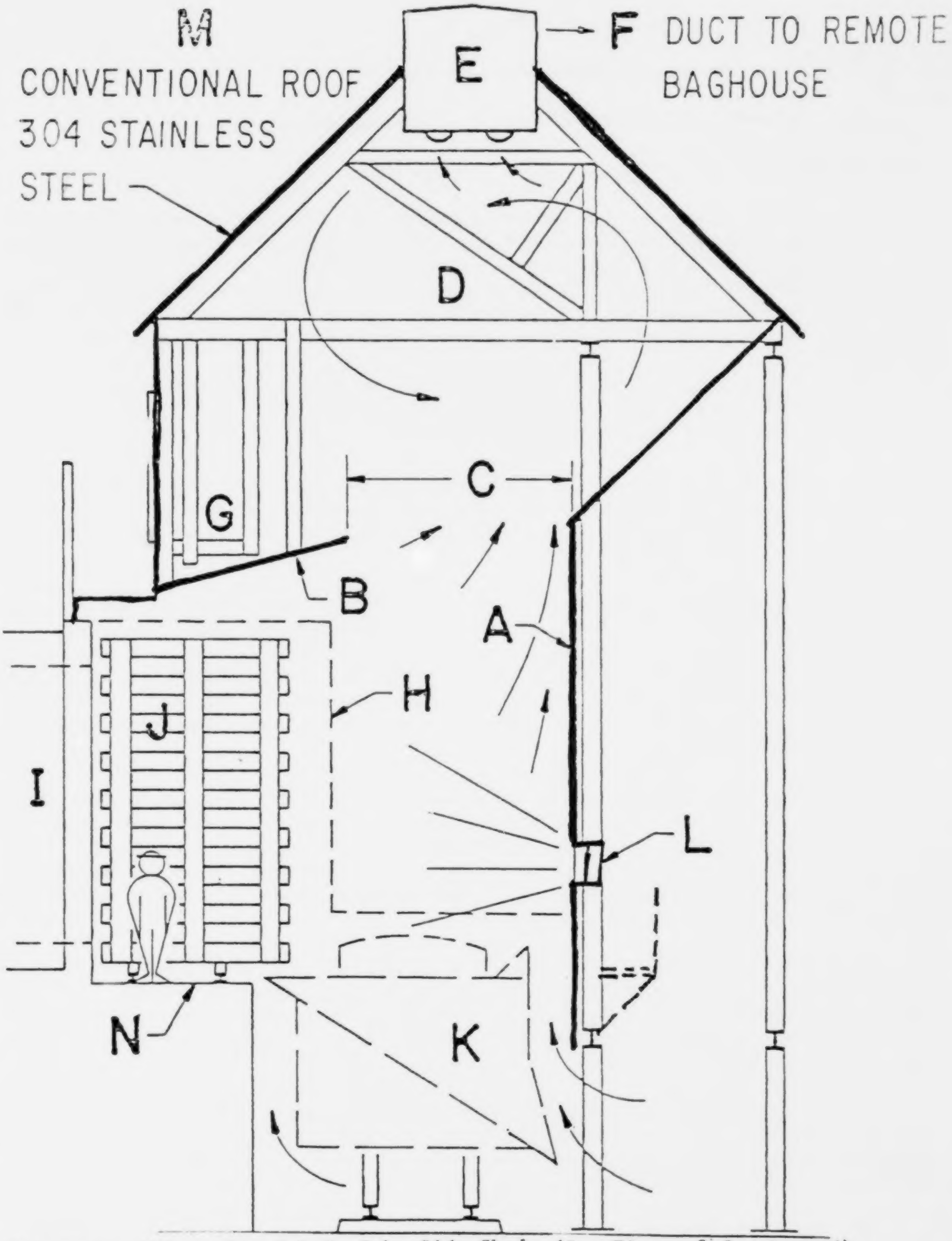
M
CONVENTIONAL ROOF
304 STAINLESS
STEEL
E
F
DUCT TO REMOTE
BAGHOUSE
D
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Figure 1. Mikropul - G.L.C. Coke Side Shed (See Figure 3 for Legend)

6. No loss of coke production.
7. Existing hot car equipment can be used.
8. No modification to battery or track required.

Some of the main disadvantages were as follows:

1. Solve the air pollution problem but create a water treatment problem. The wet precipitator required four (4) to seven (7) gallons per 1,000 CFM to operate using a blowdown rate of about 10%. A 200,000 CFM precipitator would require pumping approximately 1,000 to 1,500 GPM in its liquid circuit and a blowdown of 100 to 150 GPM requiring final clean-up. Water treatment was every expensive.
2. The wet precipitator, while being an excellent collecting device with very high efficiencies, was very expensive from the capital investment standpoint.
3. The shed allowed the large particulate to fall out onto workers under the shed during pushing. This was large particulate not considered inhalable but could get into shirt collars, etc., and was considered tolerable but annoying.
4. Particulate also settled out on the heat shield shown in Figure 1 and this had to be manually vacuumed or cleaned off every few months.
5. During periods of windy or breezy weather depending on wind direction, a wind tunnel effect could be created in the shed causing end blowout or spillover causing a visible emission during this period while pushing.
6. The wet precipitators suffered severe corrosion problems after several years of operation. This was due generally to lack of attention to the operation of the water treatment system associated with the unit. The precipitators were all constructed of mild steel with protective coatings but pH had to be controlled to keep the units from corroding away.

In general, the MikroPul-Great Lakes Carbon shed systems have proven very satisfactory over a period of several years of operation. They have proven to be very reliable, have not interfered with coke production, have been accepted by the various pollution enforcement agencies, and have had no objections from the unions working with them.

One major steel corporation, after trying almost every other type of system available at least once or twice and making what they considered a complete evaluation, has decided to install eleven (11) sheds at four (4) different plant locations.

On the shed systems presently being installed, changes have been incorporated into the design to overcome most of the objections mentioned previously. These changes are as follows:

1. Pulse-jet type baghouses or fabric filters are being used as the particulate collection device instead of the wet precipitator. This eliminates the water treatment and corrosion problems and reduces the capital cost of the system considerably. I would like to point out that only the front half particulate is being guaranteed regarding outlet emissions from the baghouse on the sheds. In recent years we have installed several baghouses on coke pushing emission systems with only having to guarantee the front half. Evidently the steel companies and coke producers, in working out their various agreements, have decided not to include the back half or condensables as particulate.

2. Secondary sheds or tunnels are being installed between the end of the primary shed and the quench tower to eliminate end blowout during windy weather.

3. Higher air volumes are being used to increase face velocities, give better capture, and quicker evacuation of the shed.

4. Vacuum systems are being installed to ease the clean-up job on the heat shield as shown in Figure 1.

The above changes help solve most of the problems encountered with the first MikroPul shed and precipitator systems.

MikroPul installed and has in operation three (3) pulse-jet baghouse systems on coke pushing operations in the United States. These systems have been in operation since July 1979, or over two years each, and have been working well. No bag changes to date and no substantial operating problems.

As I mentioned earlier in this paper, it was thought by both the steel industry and the baghouse manufacturers that the soot, tars, hydrocarbons, etc., emitted from "green" pushes would be detrimental to the operation of a baghouse. However, the capital cost of precipitators plus the very serious objections and cost of water treatment led MikroPul to try pulse-jet fabric filters on this application. We had considerable experience in dry scrubbing in the aluminum industry where hydrocarbons and light loadings of tar particles plus other gaseous condensables were involved. By properly coating or conditioning of the filter bags and continuing to do so, these elements were never allowed to impinge on the fabric but only on the dust coat itself allowing a pulse-jet fabric filter to be used successfully. Having over 12,000,000 CFM of successful operating experience in the aluminum industry, this same basic precoat technology was applied successfully to coke pushing operations.

The first MikroPul systems that were installed on coke pushing had a complete pre-coat and recycle system to continuously inject a pre-coat material to the baghouse. We have recommended a 200 mesh agriculatural limestone be used as a pre-coat. Subsequent experience has shown that continuous precoat is not necessary. The larger particulate that is captured by the pushing emissions, that is the coke fines, fly ash, soot, etc., is sufficient to act as a pre-coat and no addition is necessary. MikroPul's experience in applying pulse-jet baghouses to coke pushing applications is to apply an initial pre-coat to the virgin fabric filter bags of 200 mesh agricultural limestone. After this initial pre-coat, no further pre-coat is necessary. The collected dust from the pushing operation will act as the pre-coat. However, the cleaning of the pulse-jet collector must be carefully controlled so as to not overclean the unit.

Particulate testing run by third party independent testing companies show that outlet loadings of .01 or less can be achieved by the pulse-jet units. The recommended air-to-cloth ratio is about 6:1 (6 CFM per square foot of fabric). The fabric filter will operate at between 3" and 6" w.g. across the fabric. Bag life to date is over two (2) years and we would expect an additional two (2) years on this type of operation.

A third generation of shed has now been developed which combines the baghouse and shed into a single integral unit. The baghouse, which on previous installations had to be located remote from the shed requiring considerable runs of very large ductwork and extensive support towers and foundations, has now been made an integral part of the shed, eliminating all the ductwork, foundations, towers, etc. This is illustrated in Figure 2.

This concept, where applicable, would reduce the capital investment considerably and definitely reduces the horsepower consumption drastically. As an example, a typical pair of batteries operating under a shed would have 600 to 700 feet of ductwork inside the shed. Depending on the baghouse location there would be an additional 200 or 300 feet of ductwork outside the shed for an overall duct length of close to 1,000 feet. The fans sized for this type of system would normally be set up to operate at 18" to 20" w.g. On the MikroPul-Patton integral-type system, the total system static would be approximately 8" w.g.

CONCLUSION

It is evident even at first glance that this new technology will considerably reduce the capital cost of coke side sheds and also the operating costs. We feel this is a step in the right direction.

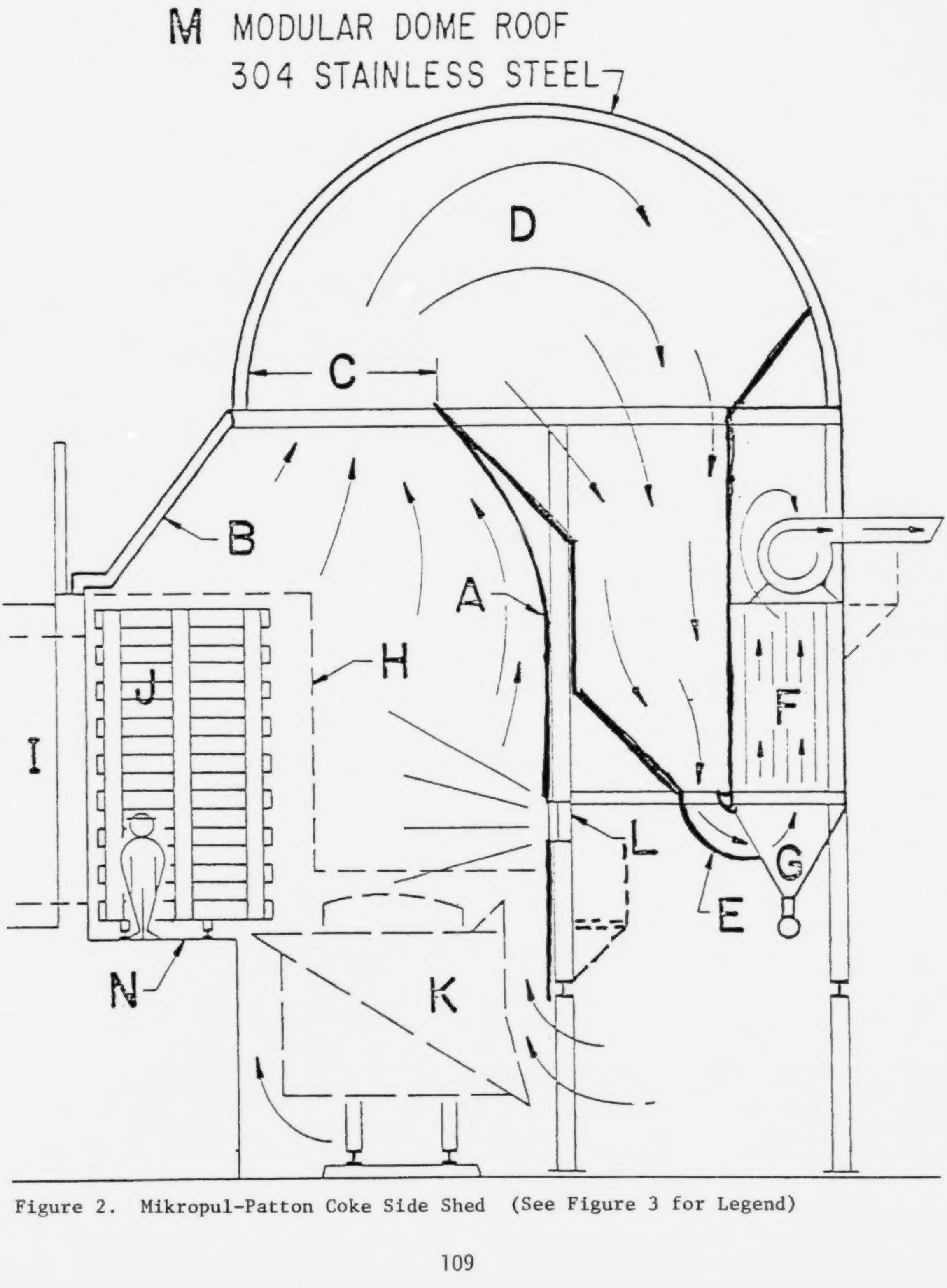
M MODULAR DOME ROOF
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Figure 2. Mikropul-Patton Coke Side Shed (See Figure 3 for Legend)

A	THERMAL WALL PANEL
B	THERMAL HEAT DEFLECTOR
C	THROAT OR STRUCTURE ORIFICE
D	CAPTURE AND EXPANSION ZONE
E	EVACUATION DUCT
F	FILTER OR CLEANING DEVICE
G	FALLOUT CAPTURE AREA
H	END WALLS
I	OVEN BATTERY
J	COKE GUIDE
K	QUENCH CAR
L	LIGHTING INSIDE OF THE SHED
M	MODULAR DOME ROOF OR CONVENTIONAL ROOF
N	BENCH AREA

Figure 3.

ARMCO'S EXPERIENCE WITH APPLICATION OF THE BUBBLE CONCEPT

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ABSTRACT

Armco's early efforts to demonstrate the advantages of the Bubble Concept led to the implementation of a comprehensive fugitive dust control program at its Middletown Works. The program was fully operational by August of 1980 and led to an acceptable alternative control plan approved by U.S. EPA in March of 1981. The prototype program has shown that significant improvements in ambient air concentrations of total suspended particulate are possible with a comprehensive fugitive dust control program and that improvements in smaller particle size fractions are realized as well.

BACKGROUND

In 1977 following the bitter battle and public rhetoric over amendments to the Clean Air Act, relationships between the U.S. EPA and the steel industry reached an ebb. The opportunity to improve upon this poor relationship came with the publication in December of 1977 of the Solomon Report, a governmental study of the many economic ills of the steel industry (1). Among those factors recognized as having negative impacts was the burden of environmental control costs to the industry. The report stated "...it may be possible to achieve our goal of a cleaner environment at a reduced economic cost if there were certain changes in the regulatory process... The EPA agrees and is willing to investigate certain areas to see if this is possible and appropriate."

In subsequent meetings between government and steel industry officials, seven areas were identified in which EPA had discretionary authority to minimize the economic burden on the industry without compromising environmental goals. Among these was the principle of total plant compliance, a concept which would allow consideration of a total plant's emissions and would provide for the flexibility to control emissions from multiple sources within a plant with the most cost-effective mix of control techniques. In 1978, this principle came to be known as the Bubble Concept, reflecting the idea that an imaginary bubble could be placed over an entire plant complex to allow consideration of the complex as a single source.

In late 1977 and early 1978, Armco had begun to assemble data and information which supported the position that controlling fugitive dust sources would be more effective and less costly than controlling process fugitive emission sources, which were receiving the most regulatory attention. Methods of estimating emissions of fugitive dust sources, such as traffic on paved and unpaved roads, material handling, and storage piles, had been developed by Midwest Research Institute under contract from EPA (2). A comprehensive emission inventory of Armco's Middletown Works revealed that over 60% of the plant's particulate emissions evolved from such open dust sources. Further studies of TSP ambient air data available for the Middletown area indicated significant impacts of open dust sources on areawide air quality and little impact of process related sources. It was obvious that the Bubble Concept provided the means for focusing on fugitive dust sources as an alternative to process fugitive emissions, and Armco campaigned actively for the adoption of a policy to provide for its inclusion and use in state implementation plan revisions.

A proposed Bubble Policy Statement was published by the U.S. EPA in the January 18, 1979, Federal Register. Although the statement encouraged states to adopt Bubble Concept provisions, it categorically excluded open dust sources from any plans for alternative considerations on the basis that emissions from such sources could neither be quantified nor be modeled with sufficient degrees of accuracy. This exclusion effectively eliminated any utility of the concept for the steel industry and Armco because of the significance of the particulate problem and the relationship of that problem to open dust sources. It became apparent that a major full-scale demonstration of the advantages of the concept was required to convince authorities that the concept was valid for fugitive dust sources at a steel plant.

ARMCO'S PROGRAM

In the spring of 1979, Armco committed to a comprehensive fugitive dust control plan at the Middletown Works. The plan consisted of a seven-point program with the following elements:

1. Reduction of plant vehicular traffic by installing plant perimeter parking and locker room facilities and establishing a busing program for employees and contractors.

2. Paving of unpaved roads, parking lots, and staging areas and installation of new paved roads to improve traffic flow where appropriate.

3. Cleaning of paved areas with daily use of mobile vacuum-type road sweepers and water spray trucks.

4. Treatment of unpaved surfaces with water and dust suppressant solutions.

5. Reduction of bare areas exposed to wind by planting of vegetation.

6. Surface treatment of storage piles with fixed or mobile spray equipment to minimize windblown emissions.

7. Installation of an ambient air monitoring network to gauge progress and effects of the program.

Details of this program have been reported previously (3).

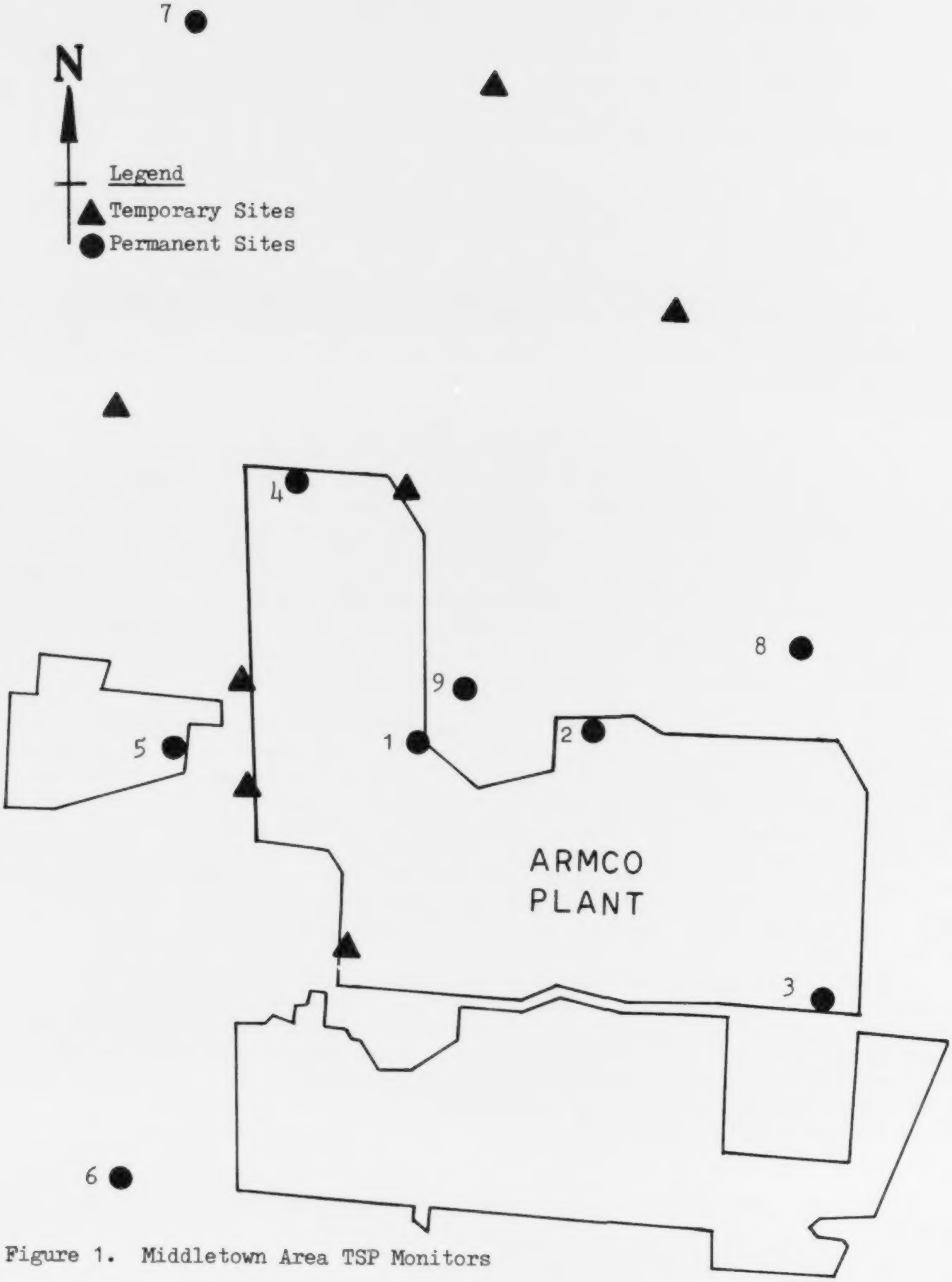
The monitoring system was made operational in August of 1979. A total of 16 monitoring sites, 6 of which were Armco-operated, were collecting data for all or part of the year preceding the complete implementation of the fugitive dust control program (Figure 1). The network provided an important data base that allowed comparison of data before and after control and that also could be used for calibration purposes for subsequent air modeling.

Following publication of the proposed Bubble Policy, Armco waged an extensive campaign to convince the U.S. EPA that open dust sources could not and should not be excluded from Bubble Concept considerations if the concept was to be useful to the steel industry. The major effort in this campaign was, of course, the commitment to proceed with the Middletown program described above at a cost of some $6,000,000, while having no guarantee of success or acceptance. However, the campaign also included efforts to convince employees, shareholders, journalists, legislators, other industrial groups, the public, and environmental groups that the concept was important to the industry and needed their support. The U.S. EPA was also kept advised of the progress of Armco's Middletown project. The final Bubble Policy was published in the Federal Register on December 11, 1979. It no longer excluded open dust sources, but it did set some rather limiting requirements for making demonstrations in cases involving such sources.

The Ohio EPA had already adopted regulations providing for Bubble Concept variances, and such a variance was requested by Armco in February of 1980. The request included a description of the plan, emission inventories, a comparative analysis of the alternative plans, ambient air data, necessary supporting information and studies, and some simplistic point source modeling to show the negligible impacts of controlling the three process fugitive sources (blast furnace cast house, open hearth, and basic oxygen shop) for which the fugitive dust controls were an alternative. The Ohio EPA asked the U.S. EPA for assistance in evaluating Armco's plan.

In the ensuing months, but prior to full implementation of the program, Armco submitted additional information to show preliminary and projected improvements with the program. More extensive modeling had been done using a CDM model and historical ambient air data for model calibration. However, U.S. EPA insisted that acceptance of the program would have to be based on a post-control analysis of the air data together with an historical trend analysis and a modeling demonstration using the more recent air data for calibration.

The Armco fugitive dust control plan was fully implemented in August of 1980.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Legend
▲ Temporary Sites
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ARMCO
PLANT

Figure 1. Middletown Area TSP Monitors

In October of 1980, Armco presented the historical trend analysis and the first two months of post-control air data. Also included were presentations of the representativeness of production and meteorology of the pre- and post-control periods. U.S. EPA was sufficiently convinced of the success of the demonstration that they announced tentative approval of the plan, contingent upon completion of the modeling demonstration and execution of all procedural requirements to convert the entire program into an approvable SIP revision.

On December 23, 1980, Armco submitted its request for a SIP revision to the Ohio EPA. It included four months of post-control air data. Several supplemental submittals were made and numerous meetings were held over the next few months to exchange and clarify data and to draft permits for all affected sources. Proposed approval of the SIP revision was published by U.S. EPA January 27, 1981, and final approval was published March 31, 1981. Table 1 chronicles the events leading to this approval.

TABLE 1. CHRONOLOGY OF EVENTS

August 1977	Clean Air Act Amendments signed
December 1977	Solomon Report issued
February 1978	Total Plant Compliance concept born
May 1978	Midwest Research Report published
June 1978	Bubble Concept terminology coined
January 1979	Proposed USEPA Bubble Policy Statement
March 1979	Armco plan committed
August 1979	Armco monitoring system operational
September 1979	Ohio EPA Bubble Concept adopted
December 1979	Final USEPA Bubble Policy Statement
February 1980	Variance request to Ohio EPA
August 1980	Armco plan operational
October 1980	Tentative USEPA approval
December 1980	SIP Revision request submitted
January 1981	Proposed USEPA SIP approval
February 1981	Ohio EPA Public Hearing
March 1981	Final USEPA SIP approval

An important part of the demonstration was a modeling exercise which was required to show that annual ambient air standards could be met under more adverse meteorological conditions and when operating at higher production rates than prevailed during the post-control period. The standard U.S. EPA model CDM was used for this purpose. Key factors in the successful application of this technique included a valid and comprehensive inventory of point source and open dust source emissions, use of an area source grid, and a successful calibration of the model through use of valid meteorological data, time-period specific emissions estimates, and a sufficient number of properly located monitors. Details of this modeling effort have been described previously (4).

RESULTS

Table 2 summarizes the total suspended particulate (TSP) ambient air data for both the year preceding the implementation of the program and the year since for the permanent stations in the Middletown area. Reductions are seen at all Middletown area stations, particularly those nearby and downwind of the plant. These reductions were accomplished at a significantly higher plant production level and under comparable meteorological conditions.

TABLE 2. CONTROL PROGRAM RESULTS

	Station	TSP Avg. Monthly Geom. Mean (ug/m^3)			
		Before Control (Aug 79-Jul 80)	After Control (Aug 80-Jul 81)	Change	% Change
1.	Reeds Yard	143	91	-52	-36
2.	Lefferson	77	62	-15	-19
3.	Oxford State	62	52	-10	-16
4.	Main Gate	74	61	-13	-18
5.	Coil Paint	66*	63	-3	-5
6.	SOS	54	47	-7	-13
7.	Hook Field	70	59	-11	-16
8.	Verity School	61	54	-7	-11
9.	Srepco	89*	75	-14	-16
	Avg. Production (T/Month)	160,780	231,777	-	+44

*Data available only for Mar 80-Jul 80

Two of Armco's monitoring stations are also equipped with size fractionating ambient air samplers (5). The SOS station is predominantly upwind of the plant, and the Lefferson station is predominantly downwind of the plant (but not necessarily at the point of its maximum impact). Table 3 shows effects of the control program for various size fractions measured at these two stations.

At the upwind station, there was relatively little change in TSP and virtually none in the fine (<2.5 um) or inhalable (<15 um) fractions. However, at the downwind station, there were significant reductions in TSP and the coarse fractions (>2.5 um) and lesser reductions in the fine fractions. It may be concluded from this data that fugitive dust control programs can also have impacts on inhalable and fine fractions of particulate matter as well as on total suspended particulate matter.

TABLE 3. CONTROL PROGRAM EFFECTS FOR VARIOUS SIZE FRACTIONS

Station Size Fraction*	Arithmetic Means (ug/m^3) Before Control (Aug 79-Jul 80)	After Control (Aug 80-Jul 81)	Apparent Reduction
LEFFERSON			
TSP	87	70	17
<2.5 um	26	23	3
2.5-15 um	25	20	5
Total IP	51	43	8
>15 <TSP	36	27	9
SOS			
TSP	53	48	5
<2.5 um	19	18	1
2.5-15 um	12	12	0
Total IP	31	30	1
>15 <TSP	23	18	5

*TSP by High Volume sampler, other fractions by Sierra Model 244 Dichotomous Sampler

OPERATION OF THE PROGRAM

The daily operation of the facilities and equipment to implement the fugitive dust control program at the Middletown Works is under the direction of a general foreman in the General Services department. He has a day foreman with sole responsibility for managing a ten-person force which operates the road sweepers and mobile spray equipment. The esprit de corps of this group was a key factor in the Middletown success.

The road sweepers are normally operated seven days per week twelve hours per day in order to provide thorough and frequent coverage of the plant's thirty miles of paved roads. The spray and flushing equipment (three separate vehicles) are operated five days per week eight hours per day.

The application of chemical dust suppressants to unpaved surfaces varies greatly with the surface in question. Some undisturbed areas require treatment only twice yearly, whereas other more active areas require twice monthly treatment. Normal application is a 1:7 solution of Coherex (Witco Chemical Co.) at a rate of about 0.1 gallon/square yard of surface, but this also varies. The annual cost of chemicals for this plant is approximately $200,000.

Operation of the fixed spray system for the coal pile can be automatically or manually activated. Normally it is programmed to operate at a specified time each day. However, it can be bypassed on wet or cold days or it can be operated more frequently in hot, dry weather. Because the spray system is designed only to provide moisture to the pile surface to prevent windblown emissions, there have been no operating problems created by excessively wet coal. The coal pile system is operated and maintained by coke plant personnel.

Maintenance problems to date have been frequent, as with most mechanical and mobile equipment, but they have not been so excessive as to cause serious operating difficulties. When one sweeper is out of service, the other must be operated more hours to cover the required road surfaces. However, the spray trucks are sufficient in number and flexible enough to provide adequate coverage when a unit is out of service.

The air monitoring network is serviced by the plant's Engineering personnel. This includes minor repairs, normal filter replacement, calibration, and data compilation. Analytical, quality assurance, audit, and troubleshooting support is supplied by the plant and Corporate Research laboratories. Corporate Environmental Engineering provided assistance for site selection and equipment acquisition and assists in the ongoing management and interpretation of air data.

SUMMARY AND CONCLUSIONS

Armco's efforts to demonstrate the benefits of the Bubble Concept as applied to iron and steel plant fugitive dust sources have spanned several years, including that period of development of the U.S. EPA's policy on the concept. The prototype program at Armco's Middletown Works has shown that significant improvements in ambient air quality are possible with a comprehensive fugitive dust control program. The improvements can be obtained with less capital and operating costs, with less energy and in less time than process fugitive emission controls. Moreover, improvements are not limited solely to total suspended particulates but also include reductions at smaller particulate size fractions.

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ENGINEERING STUDY OF ROOF MOUNTED ELECTROSTATIC PRECIPITATOR (REP) FOR FUGITIVE EMISSION CONTROL ON TWO BASIC OXYGEN FURNACES OF 300 TON CAPACITY

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ABSTRACT

A number of alternatives are available for controlling fugitive dust emissions from basic oxygen furnace operations. Use of local hoods and partial building evacuation are the common means for capturing emissions. An alternative not used in the United States, but successfully used in Japan, is roof-mounted electrostatic precipitators (REP). A study examining the feasibility of REP installation has been performed for a BOF shop with two 225 metric ton (280 ton) vessels. The purposes of the study were to determine the applicability of the devices to the BOF fugitive dust sources, examine the changes needed to existing plant facilities to interface the new equipment with the old, estimate the costs for modification of existing plant facilities and the addition of new facilities, and examine the expected performance of the proposed REPs.

In performing the study, the following steps were taken:

1. A preliminary quote for the REP was obtained from Sumitomo Heavy Industries, Ltd.
2. The requirements for electrical power supply and spray washing system were investigated.
3. Structural reinforcement to the existing BOF building was investigated.
4. An estimate of cost to install and to operate the REP was generated.
5. The quantity of fugitive furnace emissions escaping the building with the REPs in place was estimated.

The results of this study are presented in this paper.

1.0 INTRODUCTION

The conventional technique for controlling secondary emissions from existing BOF facilities is to provide local hoods at each source. This paper examines the alternative of installing roof-mounted electrostatic precipitators (REP). It presents a study which examined the feasibility of such an REP installation for an existing plant. The purposes of the study were to determine the applicability of the devices to the BOF fugitive dust sources, examine the changes needed to existing plant facilities to interface the new equipment with the old, estimate the costs for modification of existing plant facilities and the addition of new facilities, and examine the expected performance of the proposed REPs.

In performing the study, the following steps were taken:

1. Obtain a preliminary quote for the REP from Sumitomo Heavy Industries, Ltd.
2. Investigate requirements for electrical power supply and spray washing system.
3. Investigate structural reinforcement to the existing BOF building.
4. Generate an estimate of cost to install and to operate the REP on the roof of an existing BOF building.
5. Estimate the quantity of fugitive furnace emissions escaping the building with the REPs in place.

The results of this study are presented in subsequent sections of this paper.

2.0 SUMMARY

One method of controlling secondary emissions from the operation of an existing BOF is to provide roof-mounted electrostatic precipitators (REP). This method of controlling secondary emissions has been successfully applied in Japan.

The REP is of the type which is manufactured by Sumitomo Heavy Industries, Ltd. For a typical facility which contains two BOF furnaces of 273 metric ton (300 ton) capacity each, the estimated cost, delivered and erected on site is $3,020,000 or 60 percent of the estimated project cost. The remaining costs are adsorbed primarily by structural reinforcement and modification of the existing BOF building. The total estimated project cost is $5,010,000. Estimated annual operating costs are $679,000. All costs are escalated to the third quarter of 1982.

Electrical power for the REP is supplied from the existing 4.16 KV switchgear and amounts to 189 KW. An additional 40 KW is required for the motor which drives the pump in the spray washing system. Power for the motor is obtained from the control room on the scrubber platform.

The removal of dust from the REP is accomplished by automatic washing of the collector plates. Clean water for washing is pumped from the existing separator cooling towers of the primary gas scrubbing system. Contaminated wash water drains by gravity to the existing scrubber water system, which is assumed to have the capacity of absorbing the moderate additional hydraulic loading.

The existing BOF building will require extensive bracing and reinforcement to sustain the loads imposed by the precipitators, primarily against wind loads at right angles to the building aisles. A computer analysis was performed on the existing BOF building. At crosswind speeds of 100 mph, drift of the structure may be a problem which requires further structural analysis.

The REP specifications provided by Sumitomo Heavy Industries offer a design efficiency of 91.5 percent. The critical phase of furnace operation with respect to REP performance is hot metal charging. Using emission factors and several assumptions, the inlet concentration during hot metal charging is estimated as 0.96 gram/acm (0.42 grain/acf) giving an estimated outlet concentration of 0.082 gram/acm (0.036 grain/acf) where only one precipitator receives the fumes. The range of concentrations estimated to produce 20 percent opacity at the REP discharge is 0.112 to 0.222 gram/acm (0.049 to 0.097 grain/acf). Therefore, it appears the REP installation is capable of achieving discharges of less than 20 percent opacity during hot metal charging. A number of assumptions were necessary to make these performance estimates. It is important to verify the validity of some of these assumptions prior to proceeding with an installation.

3.0 APPLICABILITY OF REPs TO STEEL FURNACE FUGITIVE EMISSIONS

The applicability of roof-mounted electrostatic precipitators to fugitive steel furnace emissions has been demonstrated, in general, by steel plant operators in Japan. Sumitomo Heavy Industries, Ltd. has many operating REP installations, some in the following plants on the indicated process sources:

1. Kawasaki Steel Corporation, Chiba Works, No. 3 Q-BOP, 2 vessels, 230 metric tons
2. Kawasaki Steel Corporation, Mizushima Works, BOF, 3 vessels, 250 metric tons
3. Sumitomo Metal Industries, Wakayama Works, BOF, 3 vessels, 160 metric tons
4. Kobe Steel, Kakogawa Works, Blast furnace cast house

REPs are also manufactured by Sumitomo Metal Mining Company. They have several operating REP installations with one at Kishiwada Steel Company on a 43 metric ton electric arc furnace shop.

The process furnaces at both Kawasaki Steel plants are closed hood design. At Chiba Works they are OG design and at Mizushima Works the Irsid-Cafl system is in use. The Chiba Works was constructed with a full furnace enclosure while the Mizushima Works has a partial enclosure i.e., tapping side and top enclosed with charging side open.

In the case of Mizushima Works, the REPs were retrofit to improve furnace fugitive emission control. The REPs supplement partial furnace fugitive controls (charging and tapping hoods in the furnace enclosures) that apparently were insufficient to meet local pollution control regulations.

The Chiba Works REPs were constructed as part of the initial plant design. These REPs also supplement local fume capture in the enclosure. Charging hoods alone apparently were believed insufficient for the more difficult fugitive fume capture from bottom blown furnaces. Very limited observations of the REPs at both Kawasaki plants indicated no emissions in excess of 10 percent opacity (individual readings) during a furnace cycle of operation.[1]

At Kishiwada Steel the primary electric arc furnace emissions are captured by a direct shell evacuation system. Control of charging and tapping emissions is achieved entirely by REPs. Some limited visible emissions data (Method 9) taken at this plant are available in USEPA Region III files.

4.0 PRELIMINARY QUOTATION FOR THE REP

Preliminary quotations were requested from both Sumitomo companies, however, only one responded in sufficient detail to satisfy the study needs. Sumitomo Heavy Industries, Ltd. supplied a quotation for a REP installation to serve a BOF facility which meets the following criteria:

Heat size	260 metric tons (285 tons) 273 metric tons maximum (300 tons)
Hot metal charge	200 metric tons (220 tons)
Production	30 to 33 heats per day or 8,500 metric tons (9,400 tons) per day
Blow rate, oxygen	570 to 600 acmm (20,000 to 21,000 scfm) normal 650 acmm (23,000 scfm) maximum
Number of furnaces	2

Field measurements at such a facility indicated that the plume from charging and tapping the furnace rose at the rate of approximately 2.7 meters/ second (9 ft/sec).

At the present time, many BOF facilities operate one furnace at a time. It is, however, possible to increase steel production by relatively minor modifications which would permit two furnace operation. For this reason, it was decided to arrange the REP so that it could accommodate the simultaneous operation of both furnaces. The cost of such accommodation, if provided in the initial design, was nominal and therefore desirable.

Sumitomo Heavy Industries furnished the specification for the REP. It includes two precipitator units that have the capability of handling a total volume 27,000 acmm (953,000 cfm). Included with the units is a set of electrical equipment including high voltage power supplies (45 KV) and water sprays for washing the plates. Spraying takes place automatically for 10 minutes per section after taking sections of the REP out of service.

The specification for the REP is similar to the units which were supplied by Sumitomo to the Chiba Works of the Kawasaki Steel Corporation. Included with the specification was a general arrangement drawing (Figure 1) that shows the REP in position on the roof of the assumed BOF facility.

5.0 ELECTRICAL POWER SUPPLY

The continuous electrical consumption for the REP, based on both precipitators operating simultaneously, is as follows:

1.	High voltage supply	170 KW	-	310 KVA
2.	Insulating fans	14 KW	-	18 KVA
3.	Area and indoor lighting	5 KW	-	5 KVA
		189 KW	-	312 KVA

The power for the REP is proposed to be connected in the existing plant to the spare housing of the existing 4.16 KV, metal-clad switchgear assembly. The existing 4.16 KV switchgear obtains its power through a 5,000 KVA transformer. Since the present load on this transformer has a reactive power factor of 0.95 the present inductive reactance would be essentially balanced by the capacitive reactance of the new load due to the REP, thereby bringing the resultant power factor to approximate unity. Because of these considerations, it was decided that the present 4.16 KV switchgear and transformer would accept the new electrical load from the REP without causing overload conditions.

The control room of the REP is of sheet metal construction with a concrete floor. It is located indoors, in the furnace aisle, at elevation 254 meters (835 feet), immediately above the storage bins for furnace additives. The room is provided with ventilation, but without air filtration equipment.

The new electrical equipment in the control room includes a 4.16 KV/480V, 500 KVA silicon transformer, low voltage switchgear and precipitator controls. The precipitator controls are furnished with the

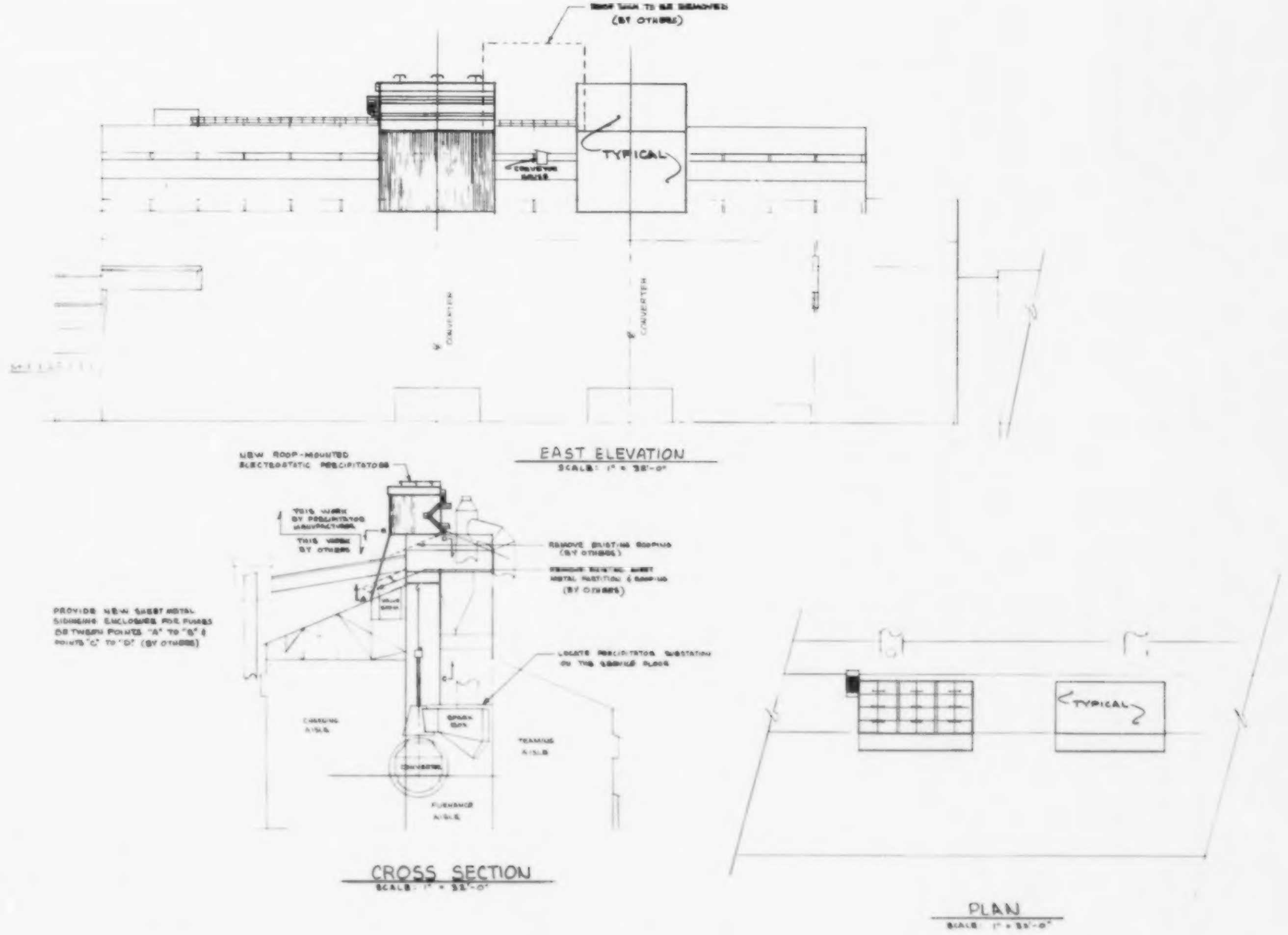
ROOF SLAB TO BE REMOVED
(BY OTHERS)
TYPICAL
CONVEYOR DRIVE
CONVERTER
CONVERTER
EAST ELEVATION
SCALE: 1" = 32'-0"
NEW ROOF-MOUNTED
ELECTROSTATIC PRECIPITATORS
THIS WORK
BY PRECIPITATOR
MANUFACTURER
THIS WORK
BY OTHERS
REMOVE EXISTING ROOFING
(BY OTHERS)
REMOVE EXISTING SHEET
METAL PARTITION & ROOFING
(BY OTHERS)
PROVIDE NEW SHEET METAL
SIDING ENCLOSURE FOR FUMES
BETWEEN POINTS "A" TO "B" &
POINTS "C" TO "D" (BY OTHERS)
LOCATE PRECIPITATOR SUBSTATION
ON THE SERVICE FLOOR
CHARGING
AISLE
SPARK
BOX
TEAMING
AISLE
CONVERTER
FURNACE
AISLE
CROSS SECTION
SCALE: 1" = 32'-0"
TYPICAL
PLAN
SCALE: 1" = 32'-0"

Figure 1. Proposed installation of roof mounted precipitator on BOF shop.

REP and include control units for operating the water valves for the automatic spray washing of the collector plates in the precipitator.

The only other electrical load imposed by the REP installation comes from the new pumps for the spray washing system. There are two pumps, one operating and one stand-by, each being driven by a 50 HP, 440V, 3 phase motor. The pumps are located on the existing scrubber platform. Power for the pumps is supplied from the existing electrical units in the control room which is also on the scrubber platform.

The existing 4.16 KV substation is located on the ground floor, immediately adjacent to the BOF building. The electrical connection between this substation and the new control room for the REP is provided by means of 4 cables, 5 KV, EPR insulated, installed in a 12.7 centimeters (5 inch) diameter galvanized conduit.

In the new control room, cable duct is proposed for connecting the switchgear to the control units which are supplied with the REP. There is electrical and key interlocking between the new 1,200 amp circuit breaker in the existing cubicle No. 7 and the new 600 amp load-break disconnect switch at the primary of the new 500 KVA transformer. The control for the new pumps has push buttons in the control center and at the motors with lock-out switches at the motors.

The lighting for the new control room and for the operating areas of the precipitators will be supplied directly from the power bus of the low voltage switchgear. The voltage of the lighting will be 277 VAC. Lighting contactors are provided in the switchgear and low voltage push buttons in appropriate locations. Indoor lighting will be low-bay mercury vapor and outdoor lighting will be sodium vapor units.

6.0 SPRAY WASHING SYSTEM

The continuous water usage in the spray washing system for the REP, based on both precipitators operating simultaneously is as follows:

1.	For sprays	1.2 m^3/min	(317 gpm)	continuous
2.	For sprinklers	.3 m^3/min	(79 gpm)	180 min/day
	Total	1.5 m^3/min	(396 gpm)	

The supply water to the precipitators is required to meet the following criteria:

Suspended solids	50 PPM, max.
Particle size	20 mesh, max.
PH	7-8
SO_4^{--}	100 PPM, max.

Cl^-	100 PPM, max.
Pressure at elevation 258 meters (847')	4 kg/cm^{2}G (131 ft.)

The water for spray washing and sprinklers is provided from an existing piping header in the present scrubber water system. Since the BOF has a scrubber on its primary gas cleaning system, the water quality from the clarifier is assumed to be generally adequate for the new service.

In the existing system, the flow rate of the water is 18.2 m^3/min (4,800 gpm). This is the design flow rate when both primary gas cleaning systems are in operation, corresponding to the simultaneous operation of both furnaces. The additional flow for the new REP system is 1.5 m^3/min (396 gpm) which is an increase of 8.3 percent over the design range for the two-furnace operation.

Thus for two-furnace operation, there is a moderate increase in flow which should be easily accommodated in the existing water system.

The spray water in the new REP is used for washing dust from the collecting plates of the precipitators. After receiving the dust from the washing operation, the water flows to the existing callow cone of the present scrubber system. The following calculations indicate the effect on the present system which results from the new contaminated water:

1. Amount of dust collected in the REP

   0.35 kg/metric ton (0.7 lb/ton) of dust from charging and tapping x 8,500 metric tons/day (9,400 tpd) of steel produced = 2,970 kg (6,580 lbs) per day. (This calculation is based on the emission factor from reference 2.)

   At a guaranteed collection efficiency of 91.5 percent, the amount of dust transferred to the water is:

   .915 x 2,970 kg/day = 2,720 kg/day (6,020 lbs/day)

2. Quality of spray water after washing (one furnace operating)

$$\frac{2{,}720 \text{ kg/day}}{1{,}440 \text{ min/day}} \times \frac{1}{1.5 \text{ m}^3\text{/min} \times 1{,}000 \text{ kg/m}^3} \times 10^6 + 50 \text{ PPM}$$

$$= 1{,}310 \text{ PPM of particulates}$$

3. Flow increase to existing water system

   The design flow to the callow cone for two-furnace operation is 10.0 m^3/min (2,650 gpm). For one-furnace operation, the flow is reduced to 5.6 m^3/min (1,470 gpm). Considering the new added flow of 1.5 m^3/min (396 gpm) from the REP, under two-furnace operation, the flow will be 15 percent above design and there will be an addition of 330 PPM to the suspended solids in the inlet water. Under one-furnace operation, the flow will be 30 percent less than design and there will be an addition of 270 PPM to the suspended solids.

Under one-furnace operation, the scrubber water system is able to accept the new added flow from the REP without exceeding the design parameters of the system. Under two-furnace operation, if such takes place in the future, the system may require modification, primarily to the callow cone, unless there is sufficient excess capacity in that unit to accept the small overload which would then occur.

The addition of water from the REP to the existing scrubber water system imposes a moderate increase in water flow and in the quantity of suspended solids. Under one-furnace operation, there is enough reserve capacity in the existing system to accept the additional loads. If two-furnace operation takes place in the future, minor additions to the existing scrubber water system may be required at that time.

The water supply and return system for the REP is shown in Figure 2. It has two pumps, one operating and one stand-by, each rated 1.1 m^3/min (300 gpm) at 100 meters (330 feet) tdh. Because of the relatively low flow and high head, it is necessary to operate the pumps at approximately 2,600 rpm and to drive them through V-belting. The pumps are located in the clean water supply system, the return of contaminated water being by gravity flow. In order to insure long life under continuous service and high rotating speed, it is recommended that the pumps be heavy-duty, Refrax lined.

The water supply system includes motor-operated valves to isolate the flow to each precipitator. These valves are controlled from a remote location in the BOF building, thereby facilitating individual operation of the REPs if desired.

7.0 STRUCTURAL REINFORCEMENT OF BOF BUILDING

The most critical consideration in the proposal to install two roof-mounted precipitators on the existing BOF building is the ability of the building to safely carry the new loads.

Figures 3, and 4 show some of the structural modifications and additions which are required to sustain the new loads. Several conditions of particular importance are as follows:

1. The load of the precipitators is carried by new steelwork into the columns on either side of the furnace aisle, per Figure 3.

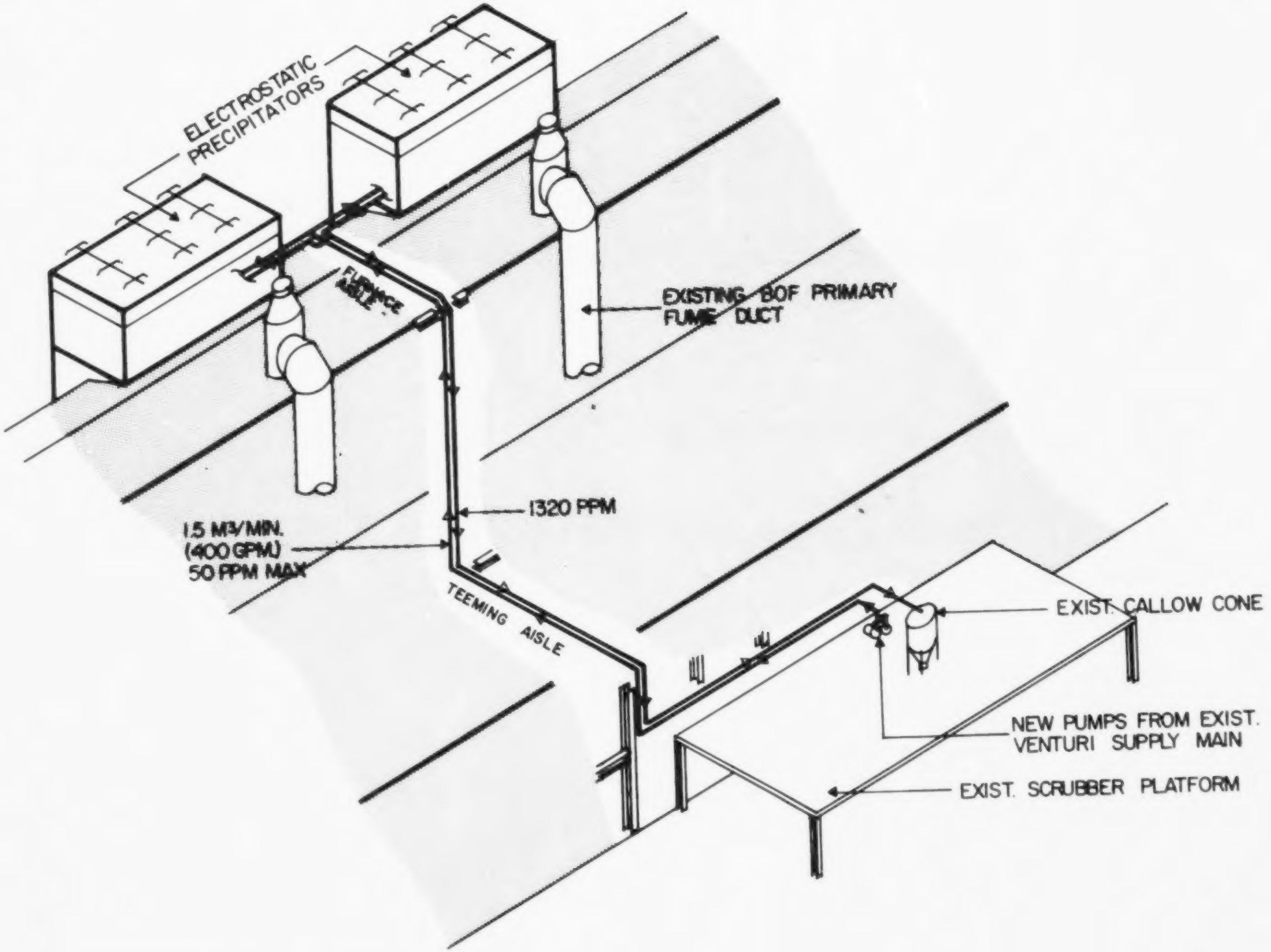
ELECTROSTATIC PRECIPITATORS
FURNACE AISLE
EXISTING BOF PRIMARY FUME DUCT
1320 PPM
1.5 M3/MIN. (400 GPM) 50 PPM MAX
TEEMING AISLE
EXIST. CALLOW CONE
NEW PUMPS FROM EXIST. VENTURI SUPPLY MAIN
EXIST. SCRUBBER PLATFORM

Figure 2. Water supply and return flow diagram.

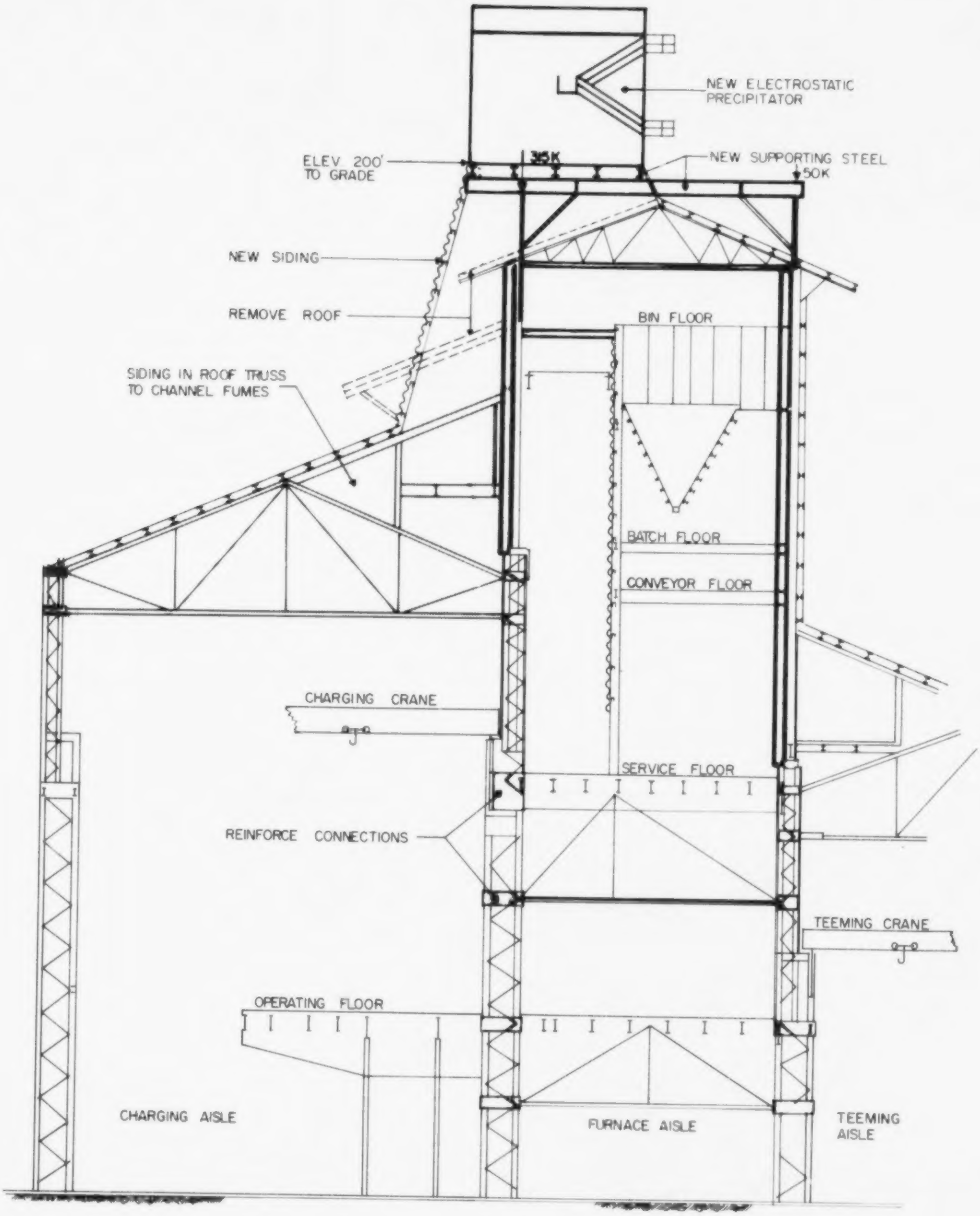
NEW ELECTROSTATIC PRECIPITATOR
ELEV 200' TO GRADE
315K
NEW SUPPORTING STEEL
50K
NEW SIDING
REMOVE ROOF
BIN FLOOR
SIDING IN ROOF TRUSS TO CHANNEL FUMES
BATCH FLOOR
CONVEYOR FLOOR
CHARGING CRANE
SERVICE FLOOR
REINFORCE CONNECTIONS
TEEMING CRANE
OPERATING FLOOR
CHARGING AISLE
FURNACE AISLE
TEEMING AISLE

Figure 3. Structural reinforcement of existing BOF building.

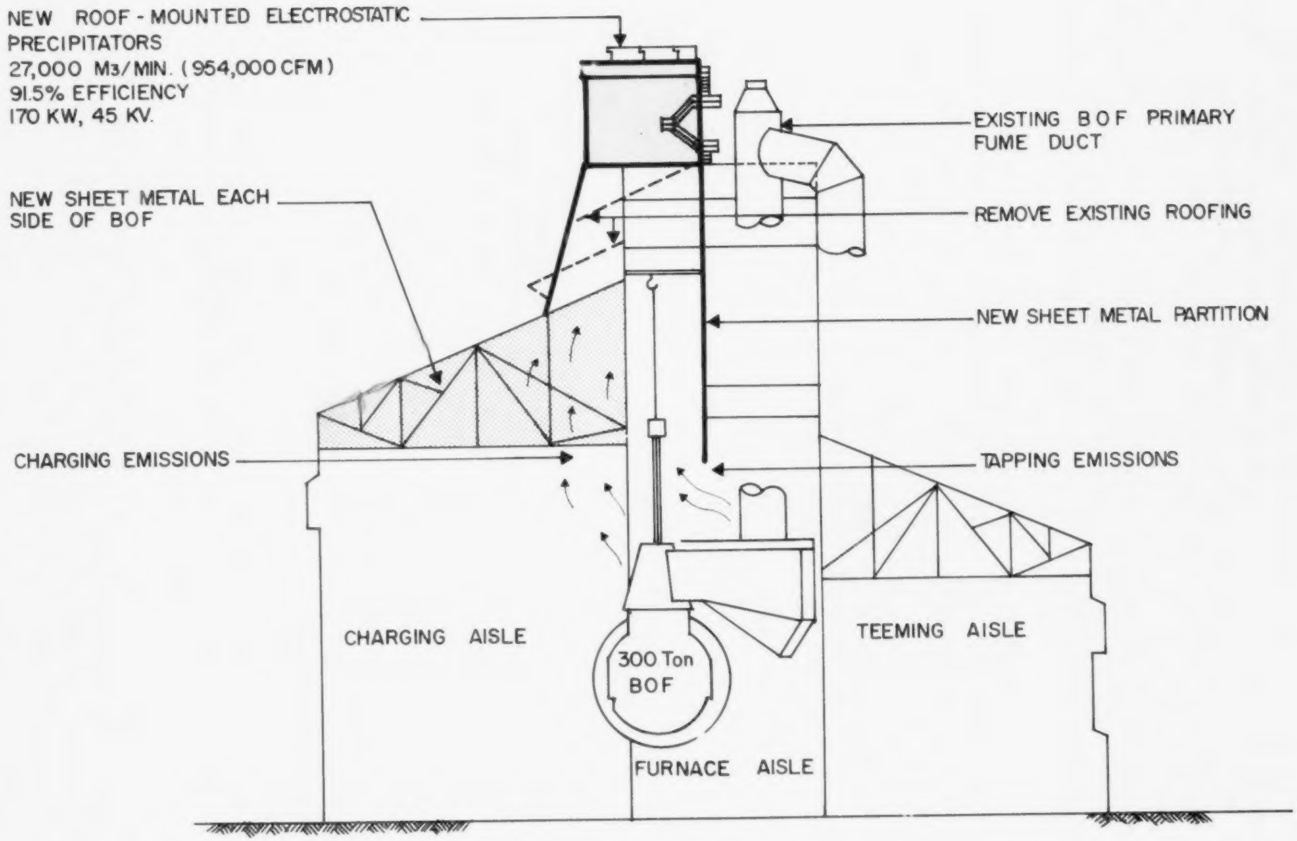
NEW ROOF-MOUNTED ELECTROSTATIC PRECIPITATORS
27,000 M^3/MIN. (954,000 CFM)
91.5% EFFICIENCY
170 KW, 45 KV.
EXISTING BOF PRIMARY FUME DUCT
NEW SHEET METAL EACH SIDE OF BOF
REMOVE EXISTING ROOFING
NEW SHEET METAL PARTITION
CHARGING EMISSIONS
TAPPING EMISSIONS
CHARGING AISLE
300 Ton BOF
TEEMING AISLE
FURNACE AISLE

Figure 4. Cross section of BOF.

Although each precipitator spans 3 columns in the north-south direction, the stringers under the precipitators are arranged to carry the loads into the end columns only. The center columns do not run to the ground but span the furnaces. It was decided, therefore, not to impose any additional loads on these center columns.

2. The dead load of each precipitator is 138.6 metric tons, thereby adding a new load to the building of 277.2 metric tons. This load may be accommodated by the existing steelwork without serious problems.

3. The most serious structural considerations are the horizontal loads which result from a design wind loading of 161 km/hour (100 mph). The horizontal loads in the north-south direction require the provision of new X bracing between column lines Nos. 10 and 12. The bracing chosen for the estimate is somewhat overdesigned and further detail analysis may result in reduction of the sections. The new structure immediately under the precipitators has horizontal and vertical wind bracing in each direction.

4. The horizontal wind loads in the east-west direction are of greatest concern, particularly in the existing steelwork above elevation 228 meters (749 feet). Below that elevation the columns are of heavy section and there is substantial wind bracing. Above that elevation, the columns are drastically reduced in size and there is relatively little wind bracing.

It should be noted that the BOF building is unsymmetrical in cross-section. Because of this condition, because the wind-loads on the new precipitators are high, and because the supporting columns have unusual configuration and size, computer "stress" runs were made using four loading cases and assuming fixed and pinned bottom connections:

1. Existing structure -- wind to the east
2. Existing structure -- wind to the west
3. Structure with precipitators -- wind to the east
4. Structure with precipitators -- wind to the west

The analysis showed that the structure below elevation 228 meters (749 feet) was adequate; however, there appeared to be excessive lateral drift at the roof line of the furnace aisle.

Because of the computer analysis, there is serious concern about the ability of the structure to accommodate the new wind loads in the east-west direction. This concern is somewhat tempered by the fact that the BOF building has extensive horizontal bracing which unifies the structure and transfers load from one column to the next. The computer analysis did not allow for this distribution of wind load on the precipitator.

For the purpose of the preliminary design and cost estimate, it was decided to reinforce the columns under the precipitators down to elevation 228 meters (749 feet). Also K-bracing is proposed above elevation 255 meters (835 feet) in order to increase lateral stiffness. It is anticipated that these measures will provide adequate reinforcement for the existing building. Nevertheless, further investigation and analysis will be required to definitely prove this contention. In making the analysis it will be necessary to re-examine certain critical structural connections to insure that they are adequate to meet the new loadings.

Figures 3 and 4 show modifications to the sheet metal siding. The purpose of the modifications is to direct the secondary emissions from the furnace into the bottom of the new precipitators. The modifications include removal of roofing in the way of the precipitators and the provision of new siding in three general areas. These are:

1. From the roof of the charging aisle to the east side of the precipitator.
2. In the furnace aisle on the west side of the lance crane.
3. In the roof trusses of the charging aisle at column lines Nos. 7, and 15.

8.0 ESTIMATE OF COSTS

The estimates of costs for installing and operating the REP are given in Tables 1 through 5. In all cases, the costs are based on the third quarter of 1982. Costs for this period were obtained by first preparing estimates for the third quarter of 1980 and then applying escalation factors. The factors are assumed to be 15 percent per year resulting in a two-year value of 32 percent.

The estimates for electrical, process piping and structural reinforcement are given in Tables 1 through 3. In preparing them, the costs were calculated using the technical information that appears on the appropriate drawings. Each estimate includes a contingency factor of 15 percent.

The estimate for providing and erecting the precipitators is derived from cost data which is included in the specification by Sumitomo Heavy Industries. These costs were developed for the Chiba Works of the Kawasaki Steel Corporation, an REP facility which is very similar to the one under consideration. The REP costs that appear in the cost summary, Table 4, include escalation and also a 10 percent contingency factor.

In order to erect the precipitator and its supporting steelwork, access to the existing BOF building is proposed from the east side of the building. Preliminary investigations indicate that there is room at this location to position a crane for direct lifting and mounting of fabrications and components. There will be some interference with railroad movements on

TABLE 1. ELECTRICAL INSTALLATION COSTS FOR ROOF MOUNTED ELECTROSTATIC PRECIPITATOR

1.	Air circuit breaker, including controls	$ 22,000
2.	Equipment in electrical equipment room	67,000
3.	Electrical cable	10,500
4.	Conduit and fittings	16,000
5.	Starters and controls	3,500
6.	Lighting	9,000
7.	Labor to install switchgear, items 1 and 2	67,000
8.	Labor to install conduit, cable and controls	90,000
9.	Engineering	5,000
10.	Contingency, 10 percent	30,000
	TOTAL	$320,000

TABLE 2. PROCESS PIPING FOR ROOF MOUNTED ELECTROSTATIC PRECIPITATOR

1.	2 Refrax-Lined pumps, 200 GPM @ 300 Ft. TDH	$31,700
2.	6" Main piping	15,000
3.	4" Branch piping	9,800
4.	Foundation & Installation of Pumps	5,000
5.	Crane Service	8,500
6.	Spares 2 percent	1,400
7.	Engineering 10 percent	7,000
8.	Contingency 15 percent	11,600
	TOTAL	$90,000

TABLE 3. STRUCTURAL REINFORCEMENT COSTS FOR ROOF MOUNTED ELECTROSTATIC PRECIPITATOR

1.	Precipitator support framing, 70 tons	$ 185,000
2.	Column reinforcing, 150 tons	495,000
3.	Connection reinforcing	150,000
4.	Wind bracing in BOF building, 40 tons	90,000
5.	Miscellaneous framing, 20 tons	46,000
6.	Purlins, 35 tons	70,000
7.	Siding, 50,000 sq. ft.	116,000
8.	Electrical control room	33,000
9.	Remove sign	35,000
10.	Remove roofing	20,000
11.	Crane rental	100,000
12.	Contingency, 15 percent	200,000
13.	Engineering	80,000
	TOTAL	$1,620,000

TABLE 4. INSTALLATION OF REP--SUMMARY OF CAPITAL COSTS

1.	Roof mounted electrostatic precipitator materials, fabrication and engineering[2] [3]	$2,090,000
2.	Shipping from Japan	40,000
3.	Field erection of REP	890,000
4.	Electric power supply	320,000
5.	Process piping	90,000
6.	Structural reinforcement of BOF building and local hooding	1,620,000
	TOTAL INSTALLED COST	$5,050,000

Notes:

1. Costs given for the 4th quarter 1982. Calculated using January 1981 costs and adding 32 percent for inflation.
2. Cost based on information from Sumitomo Heavy Industries, Ltd.
3. Costs include spare parts.

TABLE 5. INSTALLATION OF REP--OPERATING COSTS

1.	Maintenance, 2 percent of installed cost	$100,000
2.	Operators, 1 man per shift @ $40,000*	160,000
3.	Electrical power at $0.05 per KWH	83,000
4.	Service water at $.25 per 1000 gal.	36,000
5.	Depreciation, 20 year straight line	250,000
6.	Insurance, 1 percent of investment	50,000
	TOTAL ANNUAL OPERATING COST	$679,000

*Labor cost includes 25 percent fringe benefits, escalated to 3rd quarter 1982.

the tracks at ground level, but this was not deemed to be an insurmountable problem.

In general the costs were calculated using conservative methods of costing as well as conservative values for escalation and for contingencies. Thus, it is reasonable to utilize the cost values of $5,050,000 for installation and $679,000 for annual operation.

9.0 EXPECTED PERFORMANCE OF REPs

With respect to performance of the REPs, the critical furnace operation is expected to be hot metal charging. Depending on scrap quality and its impurities, hot metal charging is expected to provide the most severe test of REP performance. Tapping typically generates less intensive emissions spread over a longer time than charging, but can be as high as charging on occasion. Emissions during scrap charge, turndown (for sampling and temperature measurement), puffing (during blowing), and vessel deslagging are relatively low. Provided these latter emissions are directed (by means of partitions and baffles) to the REPs, they should easily be collected.

The REP specifications received from Sumitomo Heavy Industries provides a guarantee of 91.5 percent efficiency when the inlet concentration exceeds 0.4 gram/Nm^3 dry (0.175 grain/scf dry). At or below the design inlet concentration of 0.4 gram/Nm^3 the guaranteed outlet concentration is not to exceed 0.034 gram/Nm^3 dry (0.015 grain/scf dry).

Relating the above performance guarantee to the needs of the BOF being considered is complicated by the fact that regulations and consent decrees applying to BOF fugitive emissions are written in terms of visible emissions from the roof monitor. A theoretical basis does exist for relating emission concentration to plume opacity and that relation will be used in this examination of expected performance. However, it is important to keep in mind the conversion of concentrations to visible emissions is not a well defined science.

To estimate the performance of the REPs as applied to this plant it is necessary to make several assumptions. Should a decision to proceed with a particular REP installation be made, some additional design data to verify or alter these assumptions will have to be obtained.

1) No measurements of uncontrolled furnace fugitive emission rates were available for this study; therefore, typical emission factors for charging were assumed.

2) No measurements of gas flow rate discharged from the roof monitor were available for this study. For the purposes of these calculations, the gas rate specified for the precipitator design (based on Japanese plant experience) was assumed to be the rate of gas discharge during hot metal charging operations.

3) The upper building (within the partition walls) will act as a reservoir for the sudden fume emissions from hot metal charging. It is desirable to maintain a minimum time for hot metal charging, assumed to be two minutes. When coupled with the reservoir effect, it is assumed the hot metal charging emissions will pass through the precipitators over a three-minute period.

4) It is assumed that all the hot metal charging emissions from charging one furnace will pass through one precipitator. (As will be shown later it is desirable to divert, actively or passively, some portion to the other precipitator to reduce the dust load on a single precipitator.)

Using the above assumptions, the following calculations estimate the performance of the REP installation during hot metal charging (anticipated worst case). The emission factor for hot metal charging is 0.2 kg/metric ton (0.4 lb/ton) of hot metal poured.[2] For a hot metal charge of 195 kg (215 tons) the particulate charging emissions are given as:

195 tonnes (0.2 kg/tonne) = 39 kg

The concentration of emissions entering the single REP is given as:

$$\frac{39\ \text{kg/chg}\ (1{,}000\ \text{grams/kg})}{13{,}500\ \text{acms}\ (3\ \text{min/chg})} = 0.96\ \text{gram/acm}\ (0.42\ \text{grain/acf})$$

Assuming an efficiency of 91.5 percent gives an average outlet concentration during the hot metal charge of:

$$(1.0 - .915)(0.92) = 0.082\ \text{gram/acm}\ (0.036\ \text{grain/acf})$$

The concentration at which the plume opacity will equal 20 percent is estimated as follows:[3]

$$W = \frac{-\rho K\ \ln(I/I_o)}{L}$$

where:

W = concentration (grams/m^3)

L = light path length through plume (meters)

ρ = density of particles (grams/cm^3)

K = specific particulate volume/extinction coefficient ratio (cm^3/m^2)

I/I_o = light transmittance

For this case the variables having the following values:

L = 10 meters (distance across top of REP west to east)

ρ = 5 grams/cm^3 (iron oxide)

K = 1 to 2 cm^3/m^2 (iron oxide, mass mean radius of 5 microns, geometric standard deviation of 3 to 4)

I/I_o = 0.8 transmittance for 20 percent opacity

Therefore,

$$W = \frac{-5\ (1\ \text{to}\ 2)\ln\ (0.8)}{10}$$

$$= 0.112\ \text{to}\ 0.223\ \text{gram/acm}$$

$$= 0.049\ \text{to}\ 0.097\ \text{grain/acf}$$

The estimated outlet concentration based on 91.5 percent efficiency is 0.082 gram/acm (0.036 grain/acf). On a theoretical basis the REP installation appears to be able to achieve a discharge opacity less than 20 percent during hot metal charging. The cautions with respect to the estimating methodology must be recalled at this point. However, the hot metal charge represents the most difficult collection problem, and the other portions of the furnace cycle should be much better in terms of visible emissions.

An additional essential point of discussion with respect to performance is that Sumitomo Heavy Industries recommends the use of a local secondary hood (probably a charging hood) to reduce the total load of particulate going to the REP during charging, if it is desired to maintain 0.034 gram/Nm^3 (0.015 grain/scf). The two BOF installations of Kawasaki Steel do have this feature. The Japanese also state that lack of a local secondary hood will cause dirtier in-plant conditions than in their plants due to dust fallout. However, one would not expect the REPs to substantially alter the in-plant conditions as compared to present operations, which are assumed to have no secondary control. Should lower discharge concentrations be desired during hot metal charging two alternatives are possible. As was suggested previously in this section, provisions can be made to divert a portion of the charge emissions to the adjacent REP by means of partitions and baffling. A fan assist might even be tried. The second alternative is to provide larger REPs with higher efficiency than those in the specifications. This latter alternative is consistent with the Japanese recommendation of larger REPs if no local secondary hoods are provided.

10. ACKNOWLEDGEMENT

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1. Trip Report. Kawasaki Steel Corporation. Chiba Work, Mizushima Works. Research Triangle Institute. September 25, 26, 1979.

2. Cuscino, T. A., Jr. Particulate Emission Factors Applicable to the Iron and Steel Industry. Midwest Research Institute, Kansas City, Missouri. EPA-450/4-79-028. September 1979. p. 27-31.

3. Ensor, D. S., and M. J. Pilat. Calculation of Smoke Plume Opacity from Particulate Air Pollutant Properties. Journal of the Air Pollution Control Association. Volume 21, Number 8. August 1971. pp. 496-501.

DEMONSTRATION OF THE USE OF CHARGED FOG IN CONTROLLING FUGITIVE DUST FROM A COKE SCREENING OPERATION AT A STEEL MILL

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ABSTRACT

TRC-Environmental Consultants, Inc. (TRC) has been contracted by the Industrial Environmental Research Laboratory of the Environmental Protection Agency at Research Triangle Park, North Carolina (EPA/IERL-RTP), to test a commercially available electrostatically charged fogger on several large-scale industrial sources within the iron and steel and sand and gravel industries. This paper discusses tests conducted at a coke screening operation at a steel mill. Tests were run with no fog, uncharged fog, negatively charged fog, and positively charged fog. Data analysis indicates a doubling in total suspended particulate control efficiency when a positively charged fog was used relative to uncharged fog. For the same case, removal efficiency for particles less than 16 μm improved 2.5 times.

INTRODUCTION

Although the charged fog concept of dust control has been applied to industrial sources of fugitive dust, little data are available on fogger control efficiency. To obtain such data, EPA/IERL-RTP contracted TRC to conduct a full-scale demonstration of a charged fogger on several industrial fugitive emission sources. In particular, EPA/IERL-RTP was interested in testing the largest fogger, "Fogger IV," manufactured by the Ritten Corporation,* on several sources within the iron and steel and sand and gravel industries.

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* The Ritten Corporation, 40 Rittenhouse Place, Ardmore, PA 19003

To date, four sources have been tested. The results of the testing at the first three sources (primary rock crusher, secondary rock crusher, and cast house molten iron spout hole) have been reported in previous papers* and will not be discussed herein. The intent of this paper is to present and discuss the results of the fourth fogger field test which was conducted at a coke screening operation located at Stelco's Hilton Works in Hamilton, Ontario, Canada. The field test was performed during the period of May 1-7, 1981, with a total of 51 test runs conducted. Detailed results of all four fogger field tests are contained in the draft Interim Report.**

DESCRIPTIONS OF SITE AND PROCESS

As part of the overall steelmaking process, coal is converted to coke in order to obtain a fuel which can be used in a blast furnace to provide the high temperature reducing atmosphere necessary to smelt the iron out of the ore. To accomplish this, coal is placed into large ovens and heated to drive off volatiles. The resulting product, known as coke, is then removed from the ovens and transferred via railcar to the next step of the process.

One of the subsequent steps in the process is to segregate the still warm coke into two different size categories. The coke is transferred from a conveyor belt onto an inclined vibrating screen. Pieces of coke that are larger than the pore size of the screen travel down its face and are deposited into a hopper at its end. Pieces of coke that are smaller than the pore size pass through the screen into a different hopper. Conveyor belts then transport the separated materials to the next steps in the process. At Stelco's Hilton Works, coke arrives at the screen in runs which generally last 2 to 6 minutes. The runs are usually separated by 3 to 10 minutes.

The discharge end of the conveyor belt, the shaker screen, and the hopper inlets are all located in one room. The screening operation takes place on two different levels within this room. The conveyor belt and top of the screen are on the upper level. The hoppers and bottom of the screen are on the lower level. A catwalk runs around the perimeter of the screen on the upper level. Figure 1 is a sketch of the room which illustrates these features. Figures 2 and 3 are top and side views, respectively, that provide dimensions of the important features.

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* Brookman, E., Demonstration of the Use of Charged Fog in Controlling Fugitive Dust from Large-Scale Industrial Sources. Presented at the Symposium on Iron and Steel Pollution Abatement Technology for 1980, Philadelphia, PA, November 1980.

Brookman, E., et al., Demonstration of the Use of Charged Fog in Controlling Fugitive Dust from Large-Scale Industrial Sources. Presented at the Third Symposium on the Transfer and Utilization of Particulate Control Technology, Orlando, FL, March 1981.

** Brookman, E.T. and K.J. Kelley, Demonstration of the Use of Charged Fog in Controlling Fugitive Dust from Large-Scale Industrial Sources: Interim Source Test Report (Draft), EPA Contract 68-02-3115, TD 109, TRC-Environmental Consultants, Inc. Undated.

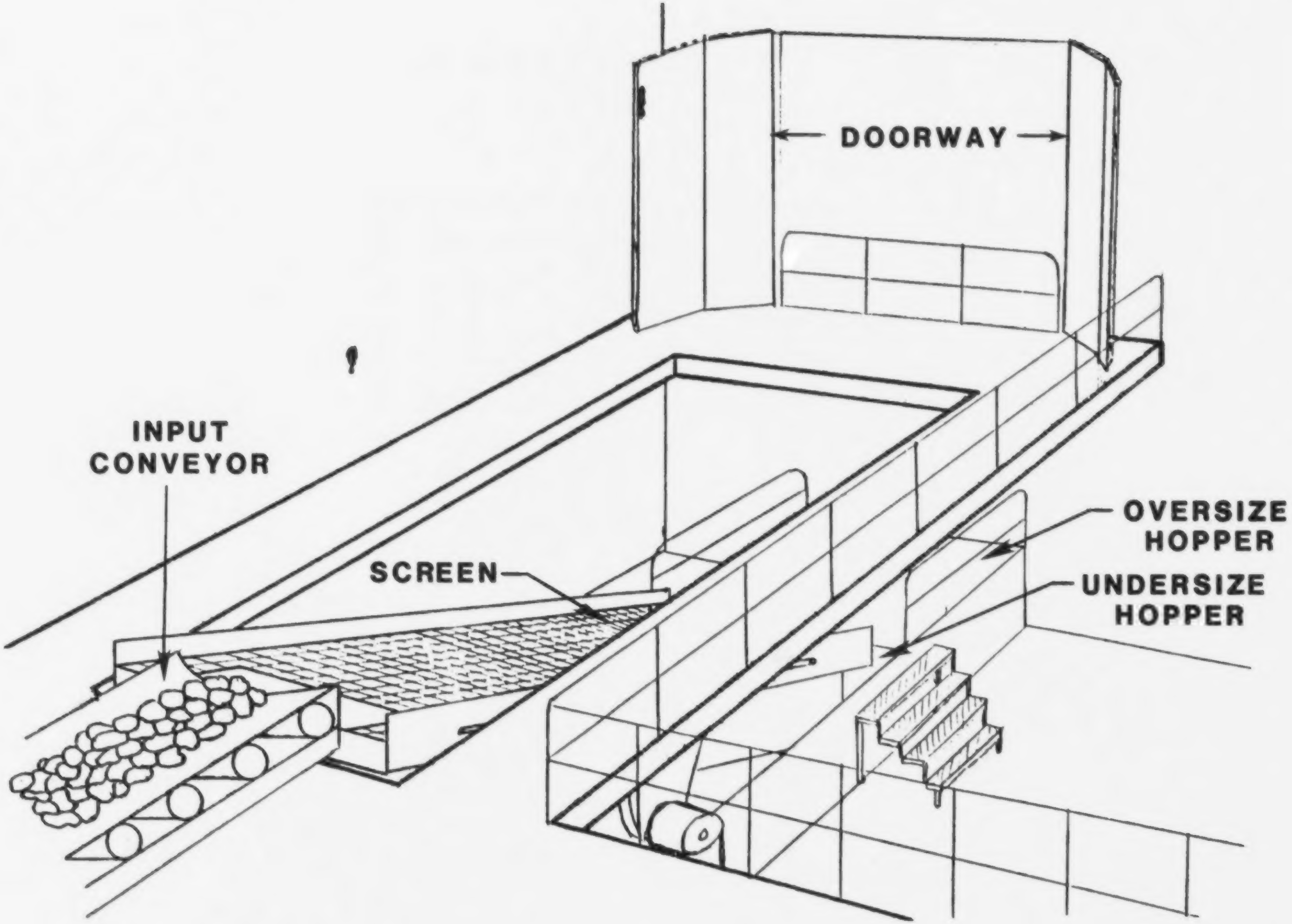
DOORWAY
INPUT CONVEYOR
SCREEN
OVERSIZE HOPPER
UNDERSIZE HOPPER

Figure 1. Coke screening operation.

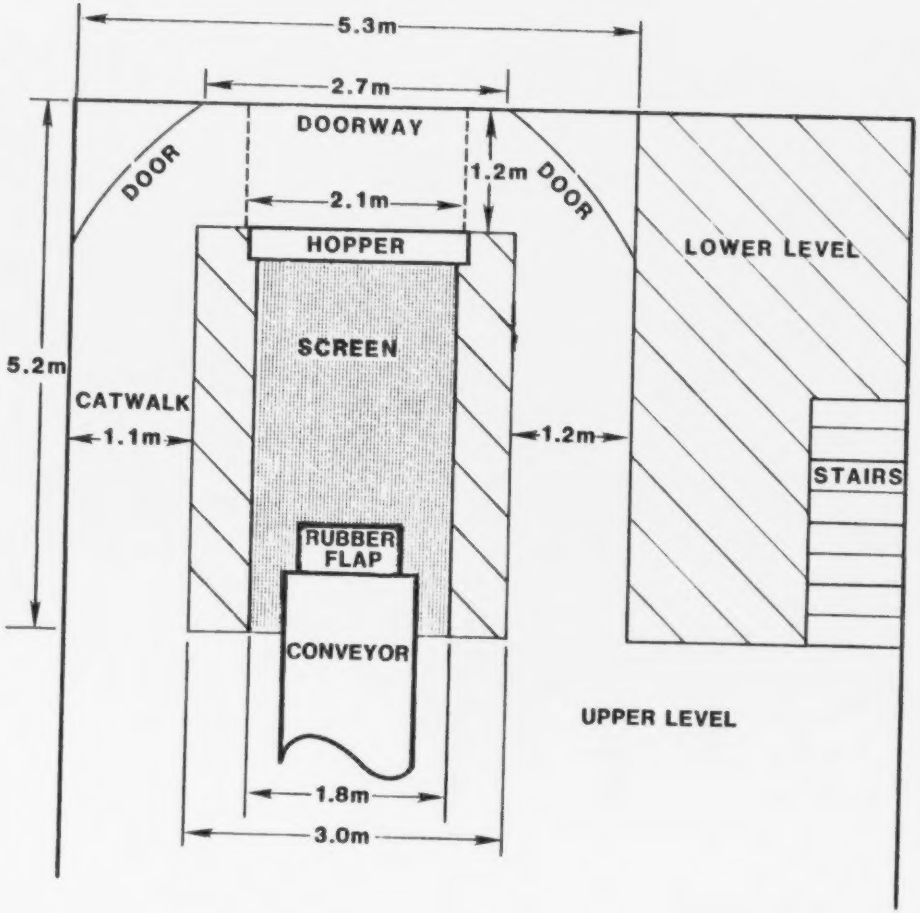
5.3m
2.7m
DOORWAY
DOOR
1.2m
DOOR
2.1m
HOPPER
LOWER LEVEL
SCREEN
5.2m
CATWALK
1.1m
1.2m
STAIRS
RUBBER FLAP
CONVEYOR
UPPER LEVEL
1.8m
3.0m

Figure 2. Top view of coke screen operation.

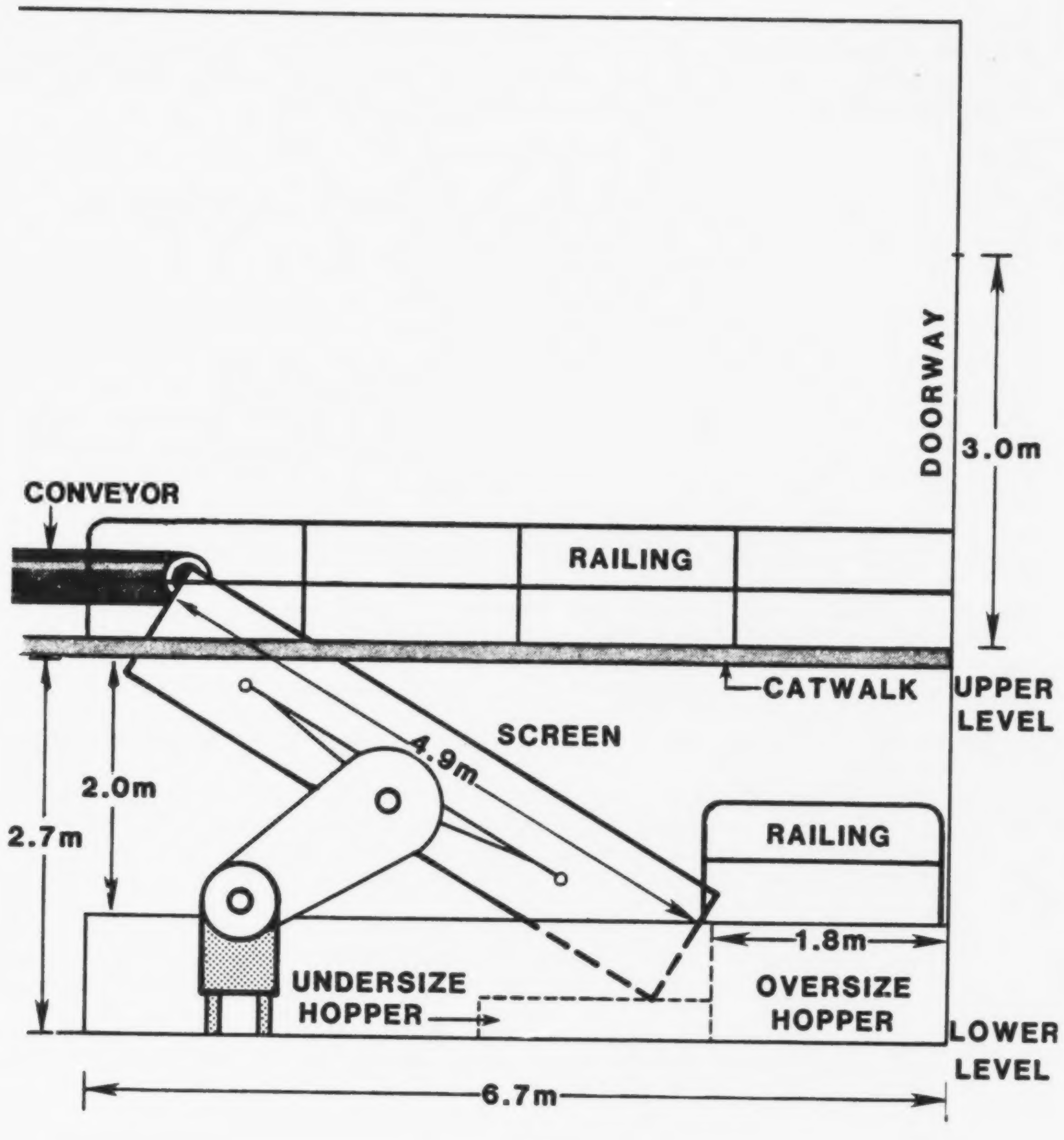
CONVEYOR
RAILING
DOORWAY
3.0m
CATWALK
UPPER LEVEL
SCREEN
4.9m
2.0m
2.7m
RAILING
1.8m
UNDERSIZE HOPPER
OVERSIZE HOPPER
LOWER LEVEL
6.7m

Figure 3. Side view of coke screen operation.

While the coke is being screened, emissions of coke dust rise up into the room from the screen and the hoppers. The majority of this dust exits the room through a large opening in the wall at the end of the screen on the second level. The rest of the dust either settles out into the room or exits the room via roof monitors or doorways.

TEST EQUIPMENT

The equipment used for the field test included two charged fog devices, five high-volume (hi-vol) particulate samplers, two size-selective inlets, and one cascade impactor. Each of these items is described below.

CHARGED FOGGERS

Two identical foggers were specially designed and fabricated for the project by the Ritten Corporation. Ritten's standard Fogger III was modified and upgraded in order to allow for variations of its operating conditions. The final configuration, designated "Fogger IV," is shown schematically in Figure 4.

In the generation of charged fog by the Fogger IV, water is atomized as it is ejected from a nozzle via a compressed air supply. As the fog leaves the nozzle, it passes through an induction ring where either a positive or negative charge, depending on the nature of the dust, is applied to the spray. A flow of air around the nozzle, provided by a centrifugal fan, projects the fog toward the dust source. A control panel, located on the back of the fogger, allows for fogger operation and parameter variability.

The requirements for and capabilities of the operational parameters are:

- Air supply to nozzle - A compressed air supply of 5.6-8.8 kg/cm^2 (80-125 psi) is required. For the tests the air was supplied by a 1.5 kW (2 hp) compressor. The air flow through the nozzle is variable from 0 to 11.3 m^3/hr (0 to 400 scfh).
- Water flow - The water supply to the fogger should be around 3.5 kg/cm^2 (50 psi) which is typical "shop" water pressure. The water flow through the nozzle is variable from 0 to 151 l/hr (0 to 40 gph).
- Power - The foggers require a power supply of 230 V, single phase, 60 Hz. The current requirements do not exceed 35 A. The power at the induction ring is 12,500 V.
- Centrifugal fan - The fan, driven by a 3.7 kW (5 hp) explosion-proof motor, operates at a maximum of 79 m^3/min (2800 scfm). The maximum output air velocity is approximately 3048 m/min (10,000 fpm). The fan flow rate is variable from 0 to 100 percent of capacity.
- Charge per drop - Assuming an average droplet size of approximately 60 μm, the average number of elementary charges per droplet was calculated to be approximately 8 x 10^4 for 75 l/hr (20 gph) water flow. This can also be expressed as a charge/mass ratio of 0.11 μC/g.

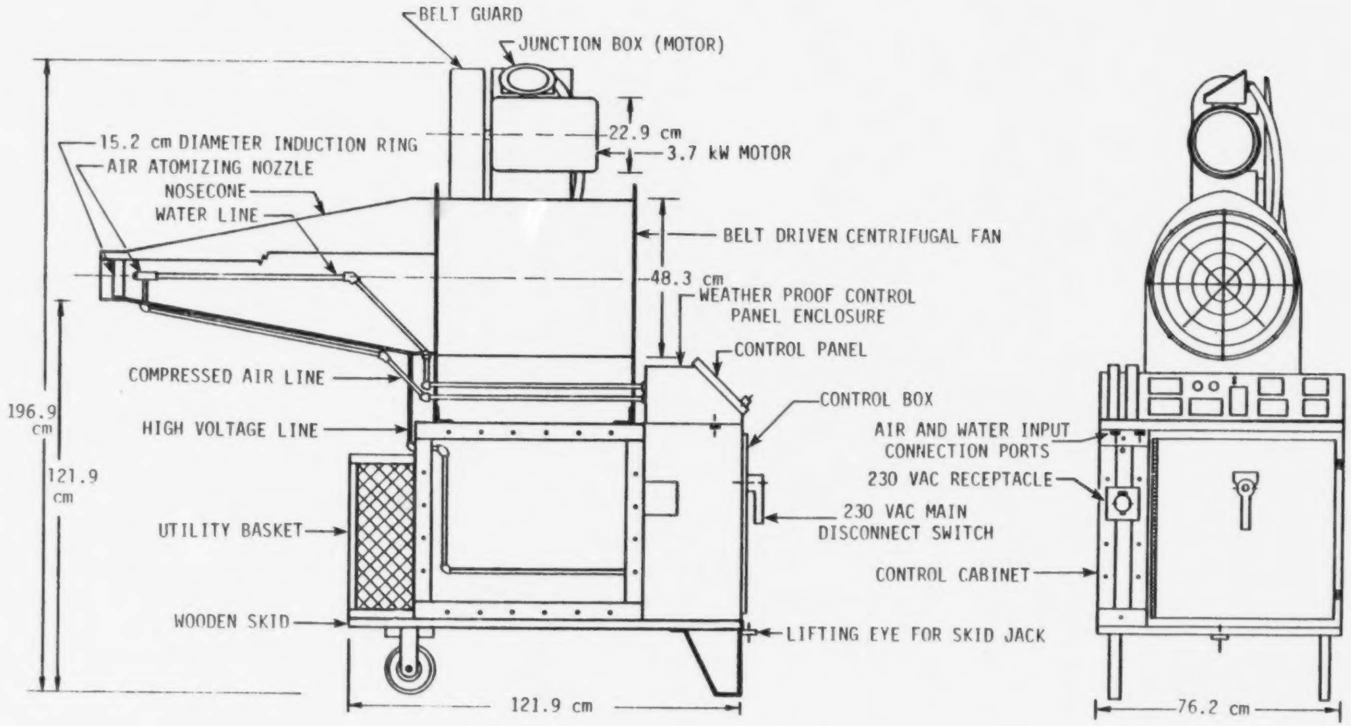
BELT GUARD
JUNCTION BOX (MOTOR)
15.2 cm DIAMETER INDUCTION RING
AIR ATOMIZING NOZZLE
NOSECONE
WATER LINE
22.9 cm
3.7 kW MOTOR
BELT DRIVEN CENTRIFUGAL FAN
48.3 cm
WEATHER PROOF CONTROL PANEL ENCLOSURE
CONTROL PANEL
COMPRESSED AIR LINE
CONTROL BOX
196.9 cm
HIGH VOLTAGE LINE
121.9 cm
UTILITY BASKET
230 VAC MAIN DISCONNECT SWITCH
WOODEN SKID
LIFTING EYE FOR SKID JACK
121.9 cm
AIR AND WATER INPUT CONNECTION PORTS
230 VAC RECEPTACLE
CONTROL CABINET
76.2 cm

Figure 4. Schematic of the Ritten Corporation's Fogger IV

SAMPLING EQUIPMENT

Hi-vol air samplers were used for the particulate measurements. The hi-vols were manufactured by Misco Scientific of Berkeley, CA, and were equipped with automatic flow control. This enabled the mass flow rate to be held constant irrespective of filter loading, atmospheric conditions, or line voltage changes. The hi-vols were operated at a nominal flow of 1.1 m^3/min (40 cfm) which corresponds to a design particulate size cutoff of approximately 30 µm.

Two of the hi-vols were fitted with size selective inlets (SSI's) manufactured by Sierra Instruments of Carmel Valley, CA. These inlets are designed to remove all particulates larger than 15 µm from the sampled air before filtering the remaining particulates onto a standard hi-vol filter.

A Sierra Instruments Series 230 four-stage cascade impactor (CI) was also used during several of the tests. When used in conjunction with an SSI, the four stages separate the collected particles into size ranges of: stage 1 - 7.2 to 15 µm, stage 2 - 3.0 to 7.2 µm, stage 3 - 1.5 to 3.0 µm, and stage 4 - 0.95 to 1.5 µm. The remaining submicron particles are collected on a backup hi-vol filter.

EQUIPMENT PLACEMENT

The equipment used for the majority of the coke screen test runs included five hi-vols (two with SSI's) and the two foggers. The five hi-vols were placed on the upper level catwalk in front of the doorway since the plume was observed to travel across this area. The two foggers had to be placed on the same side of the screen due to space limitations. One fogger was placed on the upper level and aimed down and across the screen. The other fogger was placed on the lower level about 2.7 m from the hopper. The front end of this fogger was slightly elevated so that it aimed across and above the hopper area. Figure 5 shows the positions and serial numbers of the equipment.

The equipment positions remained constant for all of the test runs; not all of the samplers were used for every run. All five samplers were used for the first 31 runs. For the next 16 runs, only four samplers were operated (standard hi-vol 7094 was eliminated) in order to allow more test runs to be conducted. The last four test runs were conducted using only one hi-vol (number 7092) fitted with both an SSI and a four-stage cascade impactor. This sampler was moved to the center of the doorway for these runs.

TEST PROGRAM AND PROCEDURE

The test program consisted of 51 runs during 6 days of testing. Included in the 51 runs were 13 uncontrolled, 8 fan only, 16 uncharged fog, 7 positive fog, and 7 negative fog. Specific test conditions are presented in Table 1.

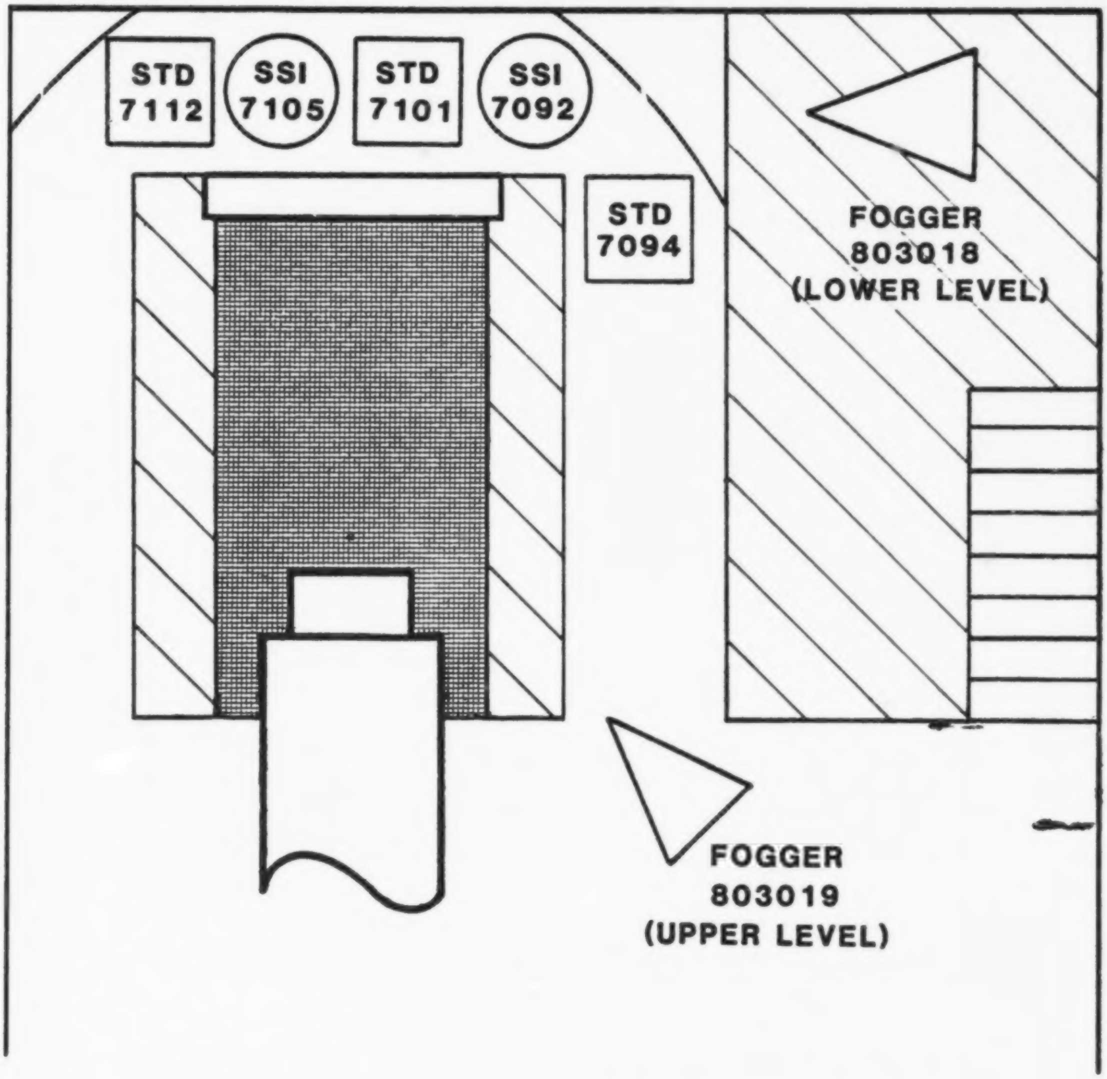
STD
7112
SSI
7105
STD
7101
SSI
7092
STD
7094
FOGGER
803018
(LOWER LEVEL)
FOGGER
803019
(UPPER LEVEL)

Figure 5. Equipment positions for coke screen.

TABLE 1. TEST CONDITIONS - COKE SCREENING OPERATION

						Fogger 803018			Fogger 803019		
Run No.	Date	Start Time	Duration Of Run (min.)	Type of Test	Equipment Positions	Water Flow (l/hr)	Air Flow (m³/hr)	Fan Speed (%)	Water Flow (l/hr)	Air Flow (m³/hr)	Fan Speed (%)
1	5-1-81	1040	5.0	Uncontrolled	*						
2	5-1-81	1100	3.5	Uncontrolled	*						
3	5-1-81	1116	4.1	Uncontrolled	*						
4	5-1-81	1210	4.2	Uncharged Fog	*	57	2.5	60	57	2.5	50
5	5-1-81	1230	4.3	Uncharged Fog	*	53	3.1	60	68	2.8	50
6	5-1-81	1247	4.6	Uncontrolled	*						
7	5-1-81	1300	3.7	Uncontrolled	*						
8	5-1-81	1318	3.5	Uncharged Fog	*	91	3.4	50	76	2.8	50
9	5-1-81	1337	4.8	Uncharged Fog	*	83	4.2	50	79	2.5	50
10	5-1-81	1402	5.4	Uncontrolled	*						
11	5-1-81	1414	3.4	Uncontrolled	*						
12	5-4-81	1300	3.2	Uncontrolled	*						
13	5-4-81	1315	6.3	Uncharged Fog	*	61	4.5	50	49	3.1	50
14	5-4-81	1330	3.1	Negative Fog	*	61	4.5	50	49	3.1	50
15	5-4-81	1345	7.3	Uncontrolled	*						
16	5-4-81	1400	2.9	Uncharged Fog	*	83	3.4	50	76	2.1	50
17	5-4-81	1440	5.1	Negative Fog	*	79	3.4	40	72	1.4	40
18	5-4-81	1450	3.8	Uncontrolled	*						
19	5-4-81	1507	3.9	Uncharged Fog	*	61	2.8	40	53	2.8	40
20	5-4-81	1520	4.9	Positive Fog	*	79	2.5	40	53	2.3	40
21	5-4-81	1535	4.4	Uncontrolled	*						
22	5-5-81	1400	3.3	Uncontrolled	*						
23	5-5-81	1422	5.4	Uncharged Fog	*	76	2.8	40	61	2.8	40
24	5-5-81	1443	3.0	Positive Fog	*	76	3.7	40	68	2.4	40
25	5-5-81	1500	4.1	Uncontrolled	*						
26	5-5-81	1511	4.6	Uncharged Fog	*	68	2.8	40	91	2.5	40
27	5-5-81	1522	3.8	Positive Fog	*	79	2.8	40	91	2.3	30
28	5-5-81	1536	4.8	Fan Only	*			40			40
29	5-6-81	0732	1.2	Fan Only	*			40			40
30	5-6-81	0812	2.9	Uncharged Fog	*	83	4.0	40	83	3.5	40
31	5-6-81	0832	2.5	Negative Fog	*	83	3.3	40	76	3.4	40
32	5-6-81	0837	3.1	Fan Only	**			40			40
33	5-6-81	0846	3.6	Uncharged Fog	**	83	3.4	40	79	3.7	40
34	5-6-81	0856	5.8	Negative Fog	**	76	3.1	40	83	3.7	40
35	5-6-81	0905	3.5	Fan Only	**			40			40
36	5-6-81	0915	2.7	Uncharged Fog	**	83	3.7	40	76	3.7	40
37	5-6-81	0925	3.2	Negative Fog	**	83	4.5	40	76	3.7	40
38	5-6-81	1003	3.1	Fan Only	**			40			40
39	5-6-81	1015	3.0	Uncharged Fog	**	76	3.7	40	91	3.1	40

NOTE: Refer to Figure 5
* Five samplers - 3 standard, 2 SSI
**Four samplers - 2 standard, 2 SSI (7094 eliminated)

TABLE 1. TEST CONDITIONS - COKE SCREENING OPERATION (Continued)

Run No.	Date	Start Time	Duration Of Run (min.)	Type of Test	Equipment Positions	Fogger 803018 Water Flow (l/hr)	Fogger 803018 Air Flow (m^3/hr)	Fogger 803018 Fan Speed (%)	Fogger 803019 Water Flow (l/hr)	Fogger 803019 Air Flow (m^3/hr)	Fogger 803019 Fan Speed (%)
40	5-6-81	1025	3.1	Positive Fog	**	79	4.2	40	87	3.1	40
41	5-6-81	1040	2.4	Fan Only	**			40			40
42	5-6-81	1055	2.6	Uncharged Fog	**	76	3.1	40	91	3.7	40
43	5-6-81	1110	6.4	Positive Fog	**	83	3.7	40	76	3.7	40
44	5-6-81	1225	2.6	Fan Only	**			40			40
45	5-6-81	1238	1.8	Uncharged Fog	**	79	3.7	40	79	5.0	40
46	5-6-81	1255	1.4	Positive Fog	**	76	4.8	40	76	4.5	40
47	5-6-71	1315	4.6	Negative Fog	**	76	4.0	40	87	4.0	40
48	5-7-81	0922	2.7	Fan Only	***			40			40
49	5-7-81	0940	2.7	Uncharged Fog	***	87	3.4	40	83	4.0	40
50	5-7-81	0956	5.6	Negative Fog	***	79	3.1	40	79	3.7	40
51	5-7-81	1015	2.2	Positive Fog	***	79	3.4	40	76	4.2	40

NOTE: Refer to Figure 5
** Four samplers - 2 standard, 2 SSI (7094 eliminated)
***One sampler - standard hi-vol with SSI and CI

The procedure was the same for each of the test runs. Pre-weighed hi-vol filters were placed in the samplers between coke runs. The samplers were simultaneously started once coke began to fall from the conveyor onto the screen and simultaneously turned off at the end of the coke run. During tests in which the foggers were used, they were started and adjusted to the proper settings prior to the start of the coke run. The hi-vol filters were immediately removed from the samplers at the end of each run and placed in envelopes. At the completion of the field test, all of the filters were returned to TRC's chemistry laboratory, desiccated, and weighed. The resulting filter loadings were then used in conjunction with the sampler flow rates to calculate particulate concentrations. These concentrations were then used directly to calculate fogger efficiency.

TEST RESULTS

Table 2 summarizes the calculated concentrations for each of the five test conditions (uncontrolled, fan only, uncharged fog, negative fog, and positive fog). The values presented were obtained by calculating the geometric mean of the data set for each hi-vol. Geometric means were preferred over arithmetic means so that the effect of outliers in the data sets was reduced. Also included in the table are the average TSP levels of the standard hi-vols and the hi-vols with SSI's. Hi-vol 7094 was not used in the standard hi-vol averages because it was not operated during all of the test runs and would thus bias some of the results.

Table 3 presents the fogger efficiencies that were calculated using the previously described geometric means for the average of the two standard hi-vols and the average of the two hi-vols with SSI's. In calculating the efficiencies, the fan-only particulate matter concentrations were used as the baseline. This was because the fans create an artificial wind effect that is constant for all conditions except the uncontrolled one. The fan air tends to redirect and, to some extent, reentrain some of the dust due to the limitations imposed by the test apparatus positioning. The particulate matter readings are spot readings only and, as noted, augmented by the fan air. They are not typical of the general work exposure levels in the facility. This phenomenon would probably not be present at a permanent installation since the fog nozzles would most probably be positioned above the source and aimed down at it. This arrangement is not possible with the experimental test equipment.

As shown in Table 3, there was a slight reduction (15 to 25 percent) in particulate matter concentrations as a result of the application of an uncharged water fog on the dust emissions at the coke screen operation. When a negative charge was applied to this water fog, the concentrations were reduced only slightly further (approximately 10 percent). When a positive charge was applied to the water fog, the concentrations were reduced an additional 30 - 35 percent. This indicates that the dust plume was primarily composed of negatively charged particles. The positively charged fog produced by the two Fogger IV's reduced the concentrations at the coke screen operation 40 to 50 percent. This level is consistent with observations which indicated that more than two foggers would be necessary to control the dust emissions from the operation.

TABLE 2. RESULTS OF FOGGER TESTING AT COKE SCREEN OPERATION: GEOMETRIC MEAN PARTICULATE MATTER CONCENTRATIONS ($\mu g/m^3$)

	Hi-Vol Designation					Avg. of 7112 and 7101	Avg. of 7105 and 7092
Run Condition	Standard 7112	SSI[a] 7105	Standard 7101	SSI[a] 7092	Standard 7094		
Uncontrolled	73022	35800	42699	26371	45609	58300	31249
Fan Only	163859	76426	143659	50514	61799	157765	63764
Uncharged Fog	147814	66128	80755	40763	56602	117098	53953
Negative Fog	117689	56403	71733	44190	77376	101413	50658
Positive Fog	100042	46459	51372	29545	37304	76598	38117

[a] <16 μm fraction.

TABLE 3. RESULTS OF FOGGER TESTING AT COKE SCREEN OPERATION: FOGGER EFFICIENCIES (%)

	Percent Reduction	
Formula Used In Calculation*	Standard Hi-Vols	Hi-Vols With SSI's
$\frac{\text{Fan Only - Uncharged Fog}}{\text{Fan Only}} \times 100$	26	15
$\frac{\text{Uncharged - Negative Fog}}{\text{Uncharged}} \times 100$	13	6
$\frac{\text{Uncharged - Positive Fog}}{\text{Uncharged}} \times 100$	35	29
$\frac{\text{Fan Only - Negative Fog}}{\text{Fan Only}} \times 100$	36	21
$\frac{\text{Fan Only - Positive Fog}}{\text{Fan Only}} \times 100$	51	40

* Inputs to formula are the geometric mean particulate matter concentrations.

The last four test runs (48-51) were conducted using a hi-vol with an SSI and a four-stage cascade impactor operated at 20 cfm. The purpose of these four tests was to obtain particle size distributions. Only four runs were conducted due to the length of time required for sample recovery. Process and plume variations would rule out determining collection efficiency reliably for this small number of tests. The results, shown in Table 4, indicate the size distribution is bimodal and that it is relatively unaffected by fogger conditions. Of the total particulate mass <16 um, 22-36 percent falls in the <1.3 μm range. Referring back to Table 2, the results of runs 1-47 showed that the <16 um fraction represents about 50 percent of the TSP, regardless of test conditions. Detailed results of this test, the earlier tests, and four additional tests now underway will be contained in the final report to be published in April 1982. The four tests now underway are co-funded with Armco, Inc.

CONCLUSIONS AND RECOMMENDATIONS

The results of the tests reported in this paper substantiate the improvement of control efficiency expected when a charged fog is used to suppress emissions from a coke screening operation. Although limited by fog generating capacity and restricted as to placement of the foggers, these tests achieved approximately a 50 percent reduction in particulate emissions. This reduction occurred across the whole particle size distribution generated by this process. It is felt that with increased fog generating capacity and optimized fogger location the level of control could be significantly improved.

Tests of charged fog for suppression of particulate should be evaluated on other fugitive emission sources to gain further experience with this technique.

TABLE 4. RESULTS OF FOGGER TESTING AT COKE SCREEN OPERATION: CASCADE IMPACTOR DATA

		Measured Concentrations ($\mu g/m^3$)					
Run No.	Test Type	Stage 1 (10.2-16µm)	Stage 2 (4.2-10.2µm)	Stage 3 (2.1-4.2µm)	Stage 4 (1.3-2.1µm)	Backup Filter (0-1.3µm)	Total (0-16µm)
48	Fan Only	12313	20746	6194	4328	16866	60448
49	Uncharged Fog	8424	10727	4545	3394	15333	42424
50	Negative Fog	11036	16022	4268	2381	9496	43193
51	Positive Fog	14088	17737	5766	3431	13066	54088

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ABSTRACT

Many of the recently constructed BOF facilities worldwide have incorporated both primary and secondary emission control systems in initial construction programs. Domestically, as a result of consent decrees and state air regulations, some older plants have retrofitted secondary emission control systems and upgraded their primary emission control systems. The effectiveness of these recent air pollution control systems varies widely. The performance of most primary control systems has been good. The largest variation in performance domestically appears among secondary control systems. This paper discusses the technology in use at some plants and reports the performance as well. Some data reported in this paper have been obtained in the process of developing background information for New Source Performance Standards for the United States Environmental Protection Agency.

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INTRODUCTION

The main goal in designing and installing a basic oxygen furnace (BOF) emission control system is to limit the particulate emissions entering the atmosphere. The degree to which this goal has been met is attested to, in part, by the decline between 1970 and 1979 in both total nationwide particulate emissions and iron and steel related particulate emissions. Nationwide estimates for various categories of emission sources are shown in Table 1. The industrial process category, which includes the iron and steel industry, has had a decline in emissions from the 1970 level of 10.2 teragrams (Tg) (11.2 megatons (ton × 10^6)) to the 1979 level of 4.3 Tg (4.7 ton × 10^6) for a decrease of 58 percent. During that time, nationwide emissions declined from 21.0 Tg (23.2 ton × 10^6) to 9.5 Tg (10.5 ton × 10^6) for a 55-percent decrease. At the same time, the iron and steel industries' emissions decreased from 1.25 Tg (1.38 ton × 10^6) to 0.47 Tg (0.52 ton × 10^6) (Table 2) for a 62-percent decrease, slightly better than the national average.[1] The BOF contribution to these emissions was 64.9 Gg (72 ton × 10^3) in 1979, which was roughly 14 percent of the iron and steel total (Table 3).[2]

BOF emissions may be divided into two categories: primary emissions and secondary emissions. Primary emissions are those generated during the oxygen blow phase of the BOF production cycle that are captured by the primary hood system. Fugitive emissions generated during charging, primary hood puffing, turndown for sampling, tapping, and deslagging are classified as secondary emissions. Virtually all BOFs presently operating in the United States are equipped with primary emission control systems. These systems are of two types: closed hood equipped with wet scrubbers and open hood equipped with either wet scrubbers or electrostatic precipitators (ESP). One open hood shop in this country has used a baghouse for primary emission control.

TABLE 1. NATIONWIDE ESTIMATES OF PARTICULATE EMISSIONS FOR 1970 AND 1979[1]

	Emissions		
	1970	1979	
Source	Tg (ton × 10^6)	Tg (ton × 10^6)	Percent change
Transportation	1.3 (1.4)	1.4 (1.5)	+0.08
Stationary source combustion	7.3 (8.1)	2.5 (2.8)	-66.0
Industrial processes (includes iron and steel industry)	10.2 (11.2)	4.3 (4.7)	-58.0
Solid waste disposal	1.1 (1.2)	0.4 (0.4)	-64.0
Miscellaneous	1.1 (1.2)	0.9 (1.0)	-18.0
Total	21.0 (23.2)	9.5 (10.5)	-55.0

TABLE 2. PARTICULATE EMISSIONS FROM THE IRON AND STEEL INDUSTRY[1]

	Emissions
Year	Tg (ton × 10^6)
1970	1.250 (1.38)
1979	0.470 (0.52)

TABLE 3. PARTICULATE EMISSIONS FROM THE IRON AND STEEL INDUSTRY--1979[2]

	Emissions
Source	Gg (ton × 10^3)
Coke	131.5 (145.0)
Blast furnace	23.6 (26.0)
Sintering	42.9 (47.3)
Open hearth	26.5 (29.2)
Basic oxygen furnaces	64.9 (72.0)
Electric arc furnaces	95.7 (105.5)
Other	89.6 (98.8)

PRIMARY EMISSION CONTROL SYSTEM

CLOSED HOOD SYSTEMS

In the closed hood system, a movable hood skirt is lowered to fit close to the furnace mouth to restrict the inflow of combustion air. Since the gases remain in a highly combustible state it is necessary to limit the amount of air infiltration downstream of the hood. Potential leakage points such as the lance port and flux chutes must be sealed and the entire system must be nitrogen purged before use. Gas flow through these systems is approximately 0.5 dscms/Mg (290 dscfm/ton) of heat size for top blown furnaces and 0.17 dscms/Mg (325 dscfm/ton) for bottom blown furnaces.

Cooling of the gas leaving the furnace initially occurs in the water-cooled hood and continues in a sparkbox or quencher where grit and coarse particles resulting from refractory wear and chunks of slag or metal are separated from the gas stream. Quenchers reduce the gas temperature to less than 93° C (200° F) and saturate the gas with water vapor.

From the quencher the waste gas flows to a high-energy scrubbing device, where removal of the fine particles occurs. ESPs are not suitable for closed hood installations because of the explosion potential inherent in the combustible waste gas stream. The most common scrubber type is a venturi with an adjustable throat. The venturi throat is opened or closed to increase or decrease gas velocity, thereby controlling pressure drop through the throat. Typical pressure drops are about 16.17 kPa (65 in. wg). The system may have multiple venturi throats, but draft is provided by a single fan.

An integral part of the scrubbing unit is a moisture-separating device to knock out drops of water carried out of the throat. This may be a series of baffles or a centrifugal chamber in which the gas rotates, causing the drops to impinge on the chamber walls. In addition, an after-cooling chamber is sometimes used where cooling water is sprayed to reduce gas temperature further. At cooler temperatures, moisture condenses, thus reducing the volume of gas to be handled by the fan. The gas-cleaning facilities are not shared between adjacent furnaces.

At present all closed hood systems in the United States flare the carbon monoxide-rich waste gas. As an alternative to flaring, the gas may be recovered in a gas-holding device and used as fuel gas for other plant operations.

Draft control in closed hood systems is critical for proper control of the combustion reaction. The systems typically include hood pressure sensors to alter draft via the adjustable venturi throat. Because the hood draft is carefully limited to maintain near-atmospheric pressure, there is a tendency for these primary systems to emit puffs of emissions at the hood-furnace interface.

TABLE 4. CLOSED HOOD PRIMARY SYSTEM EMISSION DATA--EPA REFERENCE METHOD 5

Plant	Test date	Emissions--process weight basis, g/Mg steel produced (lb/ton)	Blow time (min)	Number of cycles	Emissions--outlet concentration g/dscm (gr/dscf)	Scrubber pressure drop cm H_2O (in. H_2O)
(TOP BLOWN)						
Kaiser Steel Fontana, CA[4]						
BOF 5	12/16/78	9.30 (0.0186)	31.31	2	0.048 (0.021)[a]	175 (69)
	12/18/78	9.09 (0.0182)	29.64	2	0.046 (0.020)[a]	178 (70)
	12/18/78	8.85 (0.0177)	32.25	2	0.041 (0.018)[a]	185 (73)
BOF 6	12/14/78	7.26 (0.0145)	31.92	2	0.034 (0.015)[a]	226 (89)
	12/14/78	5.22 (0.0105)	30.28	2	0.030 (0.013)[a]	224 (88)
	12/16/78	6.97 (0.0140)	30.97	2	0.039 (0.017)[a]	221 (87)
Armco Steel Middletown, OH[3]						
	10/20/71	5.77 (0.0116)	123.75	6	0.048 (0.021)[a]	~152 (~60)
	10/21/71	7.01 (0.0141)	117.80	6	0.071 (0.031)[a]	~152 (~60)
	10/23/71	7.11 (0.0143)	124.14	6	0.046 (0.020)[a]	~152 (~60)
(BOTTOM BLOWN)						
U.S. Steel, Fairfield, AL[5 6]						
"C" Furnace	10/17/78	7.37 (0.0148)	78.50	6	0.048 (0.021)	165 (65)
	10/18/78	8.32 (0.0167)	71.10	5	0.048 (0.021)	168 (66)
	10/19/78	8.18 (0.0164)	64.30	5	0.053 (0.023)	170 (67)
"X" Furnace	12/13/78	7.24 (0.0145)	69.83	5	0.043 (0.019)	173 (68)
	12/14/78	10.23 (0.0205)	30.15	5	0.055 (0.024)	168 (66)
	12/15/78	7.48 (0.0150)	71.95	5	0.048 (0.021)	173 (68)

[a] Adjusted to oxygen blow time only.

The performance data base for closed hood systems is divided into two subsets. The first subset, presented in Table 4, is made up of tests conducted in strict accordance with EPA Reference Method 5.[3 4 5 6] Outlet concentration data for the top blown furnaces were obtained by sampling during both blowing and nonblowing periods of the furnace cycle. For Table 4, the concentrations were adjusted by calculation on the basis of assuming all particulate mass was emitted during oxygen blowing only. This assumption tends to overestimate the actual concentration that would have been measured during the oxygen blow. The three-test averages for both Kaiser Steel furnaces were below the present NSPS of 0.050 g/dscm (0.022 gr/dscf) even with the adjustment.[4] The three-test average for Armco Steel, on an adjusted basis, is 0.055 g/dscm (0.024 gr/ dscf) which is above the present NSPS.[3]

TABLE 5. SUPPLEMENTARY CLOSED HOOD PRIMARY SYSTEM EMISSION DATA

Plant	Test date	Emissions--process weight basis, g/Mg steel produced (lb/ton)	Blow time (min)	Number of cycles	Emissions--outlet concentration g/dscm (gr/dscf)	Scrubber pressure drop cm H_2O (in. H_2O)
(TOP BLOWN)						
U.S. Steel Lorain[3]						
	11/16/71	0.97 (0.0020)	97.20	6	0.007 (0.003)[a]	>173 (>70)
	11/17/71	3.93 (0.0079)	102.20	6	0.030 (0.013)[a]	>173 (>70)
	11/18/71	1.73 (0.0035)	109.10	6	0.011 (0.005)[a]	----
	11/26/72	1.04 (0.0021)	102.80[b]	6	0.007 (0.003)[a]	----
	11/27/72	0.71 (0.0014)	102.80[b]	6	0.005 (0.002)[a]	----
	11/27/72	2.40 (0.0048)	102.80[b]	6	0.018 (0.008)[a]	----
(BOTTOM BLOWN)						
U.S. Steel, Gary[3]						
East	4/17/75	13.77[c] (0.0276)	73.00	4	0.021 (0.009)[a]	160 (63)
	4/21/75	14.52[c] (0.0291)	77.00	4	0.023 (0.010)[a]	158 (62)
	4/24/75	10.49[c] (0.0210)	73.00	4	0.018 (0.008)[a]	173 (68)
West	4/22/75	5.42[c] (0.0109)	67.00	4	0.011 (0.005)[a]	160 (63)
	4/23/75	2.21[c] (0.0044)	68.00	4	0.005 (0.002)[a]	158 (62)
	4/23/75	5.96[c] (0.0119)	72.00	4	0.011 (0.005)[a]	163 (64)
Republic Steel, South Chicago[10]						
	8/4/77	6.67[c] (0.0134)	48.00	4	0.053 (0.023)	203 (80)[d]
	8/6/77	6.91[c] (0.0139)	48.00	4	0.050 (0.022)	203 (80)[d]
U.S. Steel, Fairfield[11 12]						
"U" Furnace	11/6/74	4.76[c] (0.0095)	75.00	5	0.030 (0.013)	180 (71)
	11/7/74	5.57[c] (0.0112)	64.00	4	0.032 (0.014)	175 (69)
	11/7/74	5.42[c] (0.0109)	39.00	4	0.034 (0.015)	173 (68)
"C" Furnace	9/8/78	7.79 (0.0156)	67.25	5	0.055 (0.024)	170 (67)
	9/9/78	10.68 (0.0214)	55.20	4	0.059 (0.026)	160 (63)
	9/9/78	7.91 (0.0159)	70.67	5	0.050 (0.022)	178 (70)

[a] Adjusted to oxygen blow time only.

[b] Average oxygen blow based on earlier tests.

[c] Based on 181 Mg/heat (200 tons/heat), nominal production.

[d] Design value, Reference 25.

Data for the bottom blown closed hood systems at the U.S. Steel Fairfield plant were obtained in tests in which emissions were measured during the blow period only (Table 4). As shown in the table, the average of the three runs for each furnace was nearly 0.050 g/dscm (0.022 gr/dscf).[5 6] Data from other tests conducted at this plant are presented in Table 5.

The second data base subset, presented in Table 5, is composed of a series of tests, which, for one reason or another, could not be verified as being in strict compliance with EPA Reference Method 5. This supplementary data base supports the data in Table 4. Of particular interest are the low outlet loading values reported for the U.S. Steel plants at Lorain, Ohio,[7] [8] and Gary, Indiana.[9] These adjusted values are nearly an order of magnitude less than values reported for the Kaiser and Armco plants (Table 4). The origin of these differences is not readily apparent from the available information.

With one exception, the top blown furnace closed hood primary system emission tests presented in Tables 4 and 5 demonstrate that, for those plants, the current NSPS emissions level [0.050 g/dscm (0.022 gr/dscf)] can be met, even in the worst-case situation of having all the primary emissions attributed to the oxygen blowing portion of the production cycle. Even plants that predate the current standard are able to meet it. The one top blown closed hood system that, on the adjusted basis, exceeded the NSPS limit (Armco Steel, Middletown, Ohio) did so on only one of three test runs. On an unadjusted basis, i.e., with continuous sampling from the start of the blow to the beginning of tapping, the plant complied with the current NSPS limit.

OPEN HOOD SYSTEMS

An open hood scrubber control system is basically the same as that described for closed hoods, except that the position of its hood skirt is fixed instead of movable. Since all the combustible gases are burned in the hood, no precautions against leakage into the system are necessary. Control systems may be shared between furnaces and multiple fans operating in a parallel flow arrangement can be used if desired. Gas volumes are typically 0.78 dscms/Mg (1,500 dscfm/ton) of heat size for top blown furnaces.

When a precipitator is used, gas cooling downstream from the hood skirt is achieved by use of water sprays located in the upper part of the hood. These sprays are generally controlled by time and/or temperature to turn on and off at various points in the operating cycle. The intent is to limit the gas temperature reaching the precipitator and to condition the gases with moisture for better precipitation. Maximum temperature of gases entering the precipitator is usually kept under 343° C (650° F). Flaring of carbon monoxide-rich gas practiced in closed hood systems is not necessary in open hood systems since the carbon monoxide is burned within the hood.

Because the gas temperature is relatively low during the early minutes of a blow, some plants use steam injection at the hood or spark box to achieve the desired conditioning of gases. Water sprays do not evaporate sufficiently under the low temperature conditions, and puffs of iron oxide fume are typically observed from the stack during this period. Steam injection both at the beginning and end of the blow can reduce these emission puffs.

Downstream of the sparkbox the gases are carried to an inlet plenum that distributes them to multichambered precipitators. On the outlet side of the precipitator there is usually a manifold arrangement that distributes the gases among multiple fans. The precipitators may or may not have spare capacity in terms of an extra chamber or extra collection field in the direction of gas flow. At least one spare fan commonly is available.

Performance data from the period 1975 to 1979 for open hood control systems are available. The data were obtained primarily during compliance tests and show that all the plants were within limits set by the present NSPS for BOFs (Table 6). All the tests were conducted during oxygen blowing only.

The open hood systems had no difficulty meeting the NSPS emission limits due, in part, to the dilution that results from the high evacuation rates required in these complete combustion systems. When emissions are expressed on a process weight basis, open hood systems in general do not perform as well as closed hood systems (Table 4, 5, and 6). For a given sized plant, a closed hood system allows fewer emissions into the atmosphere than an open hood plant in spite of the lower outlet concentrations associated with open hood systems.

SECONDARY EMISSION CONTROL SYSTEMS

A variety of systems are used to capture secondary BOF emissions. Many systems have been retrofitted to existing shops and are therefore unique, while others were designed as original equipment in new shops. The systems discussed are furnace enclosures (doghouses) with local hoods (Kaiser Steel, Fontana, California; and Republic Steel, South Chicago, Illinois), partial furnace enclosures with local hoods supplemented by partial building evacuation (Inland Steel number 2 BOF shop), and open primary hoods modified to facilitate secondary emission capture (Bethlehem Steel, Bethlehem, Pennsylvania; and Republic Steel, Gadsden, Alabama).

Full Furnace Enclosures

Kaiser Steel (Closed Hood, Top Blown)--

The Kaiser Steel secondary emission control system at the Fontana, California, plant controls furnace emissions (charging, tapping, puffing of the primary, and turndown), and emissions from hot metal transfer and hot metal skimming.[20]

The system has two fans each rated at 149 m^3/s (315,000 acfm) at 50 cm (20 in.) of water column and 230° C (450° F).[21] Both fans operate to provide the baghouse design flow of 283 m^3/s (600,000 acfm). Dampers are used to reduce gas flow and energy consumption when full system flow is not required. Air flow is divided among the various secondary hoods according to each operation's needs. Operations permitted to occur simultaneously depend on whether one or both furnace vessels are being used. Based on design information, hot metal charging requires the largest air flow, about three-quarters of system capacity. The Kaiser system does not permit hot metal transfer, hot metal skimming, or hot metal charging to the other vessel while one vessel is being charged. However, the system does permit oxygen blow, turndown, tapping, or deslagging of one vessel during charging of the other. Hot metal transfer

TABLE 6. OPEN HOOD SYSTEM PERFORMANCE DATA

Plant	Test date	Emissions--process weight basis g/Mg steel produced (lb/ton)	Emissions--outlet concentration g/dscm (gr/dscf)
U.S. Steel South Works, Chicago, IL[13] - Scrubber	6/27/77	1.95 (0.0039)[a]	0.0089 (0.0039)
		2.92 (0.0059)[a]	0.0086 (0.0038)
		3.45 (0.0011)[a]	0.0103 (0.0045)
		2.94 (0.0059)[a]	0.0087 (0.0038)
	6/29/77	5.64 (0.0113)[a]	0.0141 (0.0062)
		5.14 (0.0130)[a]	0.0127 (0.0056)
		3.39 (0.0068)[a]	0.0112 (0.0049)
		3.86 (0.0077)[a]	0.0101 (0.0044)
	7/1/77	5.74 (0.0115)[a]	0.0167 (0.0073)
		6.04 (0.0121)[a]	0.0165 (0.0072)
		4.41 (0.0088)[a]	0.0118 (0.0052)
		4.10 (0.0082)[a]	0.0119 (0.0052)
CF&I Steel Pueblo, CO[14] - (ESP)	4/10/78	33.38 (0.0669)[a]	0.0503 (0.0220)
	4/11/78	13.30 (0.0267)[a]	0.0224 (0.0098)
		18.71 (0.0375)[a]	0.0263 (0.0115)
	4/12/78	13.77 (0.0267)[a]	0.0222 (0.0097)
		12.55 (0.0251)[a]	0.0214 (0.0094)
Republic Steel, Buffalo, NY[15] - (ESP)	10/20/75	----	0.0275 (0.0120)
	10/21/75	----	0.0297 (0.0130)
	10/22/75	----	0.0275 (0.0120)
Wisconsin Steel, Chicago, IL[16] - (ESP)	11/10/76	~17.97 (~0.0360)	0.0211 (0.0092)
	11/12/76	~28.44 (~0.0570)	0.0302 (0.0132)
	11/16/76	~17.96 (~0.0360)	0.0216 (0.0094)
	11/18/76	~20.96 (~0.0420)	0.0263 (0.0115)
Jones & Laughlin, Aliquippa, PA[17] - (ESP)	8/10/76	6.29 (0.0126)	0.0092 (0.0040)
	8/11/76	----	0.0031 (0.0014)
Youngstown S&T, Indiana Harbor, IN[18] - (ESP) (Now J&L Steel)	6/12/78	18.64 (0.0373)[b]	0.030 (0.013)
	6/13/78	10.98 (0.0220)[b]	0.018 (0.008)
	6/14/78	13.62 (0.0330)[b]	0.027 (0.012)
Crucible Steel Midland, PA[19] (Baghouse)[c]	6/11/80	----	0.0048 (0.0021)
	6/11/80	9.40 (0.0188)[c]	0.0044 (0.0019)
	6/12/80	16.65 (0.0333)[c]	0.0073 (0.0032)
	6/12/80	14.35 (0.0287)[c]	0.0064 (0.0028)

[a] Based on 181-Mg (200-ton) nominal capacity.

[b] Based on 254-Mg (280-ton) nominal capacity.

[c] Based on 95-Mg (105-ton) nominal capacity, and 20 minute blow.

or hot metal skimming require about one-third system flow capacity and may occur at any time, providing that neither furnace is being charged.

Performance of the secondary emission control facility during single vessel operation at Kaiser was evaluated in April 1980[22] using visible emissions measurements of roof monitor discharges (EPA Reference Method 9).

These measurements have been analyzed by two methods. Table 7 presents the results analyzed according to EPA Method 9, i.e., 6-minute average opacities based on observations made every 15 seconds. The table shows the cumulative frequency distribution for 6-minute averages taken each day. On the worst day none of the averages exceeded 15 percent opacity, while on the best day none of the averages exceeded 5 percent opacity.

Table 8 presents data analyzed on the basis of average number of individual opacity observations equal to or exceeding 20 percent opacity for each segment of 21 production cycles. It is evident from the table that turndown for sampling produced the greatest number of opacity excursions at Kaiser Steel.

Republic Steel, Chicago (Closed Hood, Bottom Blown)--

Only three plants in the United States presently have bottom blown furnaces (Q-BOP). The two furnace vessels in the Republic Steel plant, East Chicago, Illinois, have a capacity of 205 Mg (225 tons). The secondary emissions system at this plant includes full-furnace enclosures with charging hoods at the front of each enclosure. There are no tapping hoods, and neither hot metal transfer emissions nor hot metal skimming emissions are ducted to this system.

Operations of the Q-BOP during charging and turndown require gas (either nitrogen or oxygen) to be blown through the tuyeres to prevent liquid metal, slag, or solids from entering and clogging the tuyeres. This purging makes capture of the secondary emissions more difficult than with top blown furnaces.

Draft for the charging hood at the Republic plant is obtained from the primary fume control system. Each furnace has its own primary gas cleaning system; however, a crossover duct between the two furnaces permits the system of the nonoperating furnace to be used for secondary emission control on the operating furnace. With both gas cleaning system fans drafting the charging hood, the flow rate is about 176 m^3/s (373,000 acfm) at 93° C (200° F) during hot metal charging.[23] During charging, turndown, and tapping, the charging hood is drafted by the scrubbing system of the nonoperating vessel. Fume capture during these operations is assisted by drafting the primary hood. Fumes captured in the secondary (charging) hood bypass the quencher and pass directly to the venturi in the scrubbing system. The design pressure drop of the venturi during furnace charging is 218 cm (86 in.) water column.

In general, the performance of the secondary emission control system at Republic Steel was poorer than the best performing top blown furnace secondary systems. Data are available for two test series, June 1979 and June 1980.[23 24]

TABLE 7. KAISER STEEL, FONTANA, CALIFORNIA[22]

Date/ opacity	Cumulative percent of 6-minute averages less than or equal to given opacity				Number of individual observations
	0	5	10	15	
4/7/80	85.0	98.5	99.8	100	1,683
4/8/80	60.1	93.2	99.4	100	2,310
4/9/80	87.3	100			2,161
4/10/80	89.1	99.3	100		1,533
4/11/80	97.9	98.7	100		1,549

TABLE 8. AVERAGE NUMBER OF TIMES PER HEAT THAT OPACITIES WERE EQUAL TO OR GREATER THAN TWENTY PERCENT

Plant		Number of heats tested	Average number of observations $\geq$20 percent opacity			
			Charging	O_2 Blow	Turndown	Tapping
Kaiser Steel[22] Fontana, CA		21	0.23	---	1.86	0.05
Republic Steel S. Chicago (Q-BOP)	1979[23]	22	2.0	1.64	3.45	7.40
	1980[24]	5	4.20	1.0	3.40	3.36
Inland Steel[26] #2 BOF Shop		6	2.7	5.5	1.7	0.17
Bethlehem Steel[29] Bethlehem, PA		11	0.09	0	0.18	0
Republic Steel[30] Gadsden, AL		42	0.48	4.57	0	0.02

TABLE 9. REPUBLIC STEEL, CHICAGO, ILLINOIS[23] [24]

Date/ opacity	Cumulative percent of 6-minute averages less than or equal to given opacity										Number of individual observations
	0	5	10	15	20	25	30	35	40	45	
6/18/79	10.3	33.5	53.1	73.7	38.6	96.4	98.3	100			1,363
6/19/79	54.6	94.3	99.0	100							1,819
6/20/79	54.4	95.9	100								1,901
6/21/79	42.2	90.0	93.1	97.2	97.9	98.7	98.9	99.3	100		1,670
6/22/79	13.5	67.8	81.8	90.3	96.6	97.3	98.8	100			588
6/2/80	61.8	96.6	97.2	98.2	99.2	99.7	100				1,241
6/3/80	21.1	53.3	75.6	86.1	95.8	98.3	99.4	100			1,765
6/4/80	64.1	96.8	99.6	100							2,448
6/5/30	52.7	79.7	86.8	91.3	94.1	97.2	98.9	99.5	99.8	100	5,675
6/6/80	24.4	30.3	95.1	99.8	100						1,174

These measurements have been analyzed by two methods. Table 9 presents results of data analyzed according to EPA Method 9, i.e., 6-minute average opacities based on observations made every 15 seconds. The table shows the cumulative frequency distribution for 6-minute averages taken each day.

No 6-minute average opacity exceeded 45 percent during the tests at Republic Steel. However, only 3 of the 10 days during which observations were made had no average opacities over 15 percent, as opposed to Kaiser where all 5 days had no average opacities over 15 percent.

Table 8 presents the same data analyzed on the basis of the average number of individual opacity observations equal to or exceeding 20 percent opacity for each segment of 27 production cycles.

From examining this plant's performance on the basis of individual cycles, it is evident that performance is characterized by extremes. One group of cycles had 0 to 6 excursions equal to or greater than 20 percent, and a second group of cycles had 19 to 36 excursions. No cycles fell between these two groups. Specific causes for this large variation have not been identified. The data also show that in many of the production cycles with a high number of total excursions, each of the cycle segments, rather than just one segment, contributes to the overall high emissions. Tapping, however, appears to produce more excursions than the other cycle segments (Table 8).

During the 1979 tests it was noted that leakage occurring on the tapping side of the furnace enclosure contributed to fugitive tapping emissions.[25] The addition of a separate tapping side hood to the enclosure might improve overall system performance.

Partial Furnace Enclosure

Inland Steel, East Chicago, Indiana (Closed Hood, Top Blown)--

The No. 2 BOPF shop at Inland Steel's East Chicago plant contains two 195-Mg (215-ton) capacity top blown furnaces. The primary gas-cleaning system is a closed hood type with venturi scrubbers.

There are two principal secondary emission control systems in this plant. One system is composed of local hoods located in the partial furnace enclosure. Fugitive emissions in the charging aisle are captured by a partial building evacuation system, which also receives emissions from local hoods at the hot metal transfer and hot metal skimming stations.

Local hoods within the partial furnace enclosure include a charging hood, tapping hood, and a wraparound hood (at the sides of the furnace) to capture puffing emissions during the oxygen blow. During charging, only the charging hood is drafted; during tapping, the tapping hood and wraparound hoods are drafted. During the oxygen blow, all three hoods are in service. Draft for the furnace enclosure secondary emission control system is induced through a venturi scrubber by a fan rated for 62 m^3/s (131,000 acfm) at 21° C (70° F).[25] Overall system pressure drop is 130 cm (51 in.) water column. This evacuation rate is not sufficient to capture all charging and furnace deslagging emissions, some of which escape to the partial building evacuation system.

The partial building evacuation system is limited to the furnace charging aisle. There is a curtain wall which prevents the charging emissions from escaping into the uncontrolled furnace aisle. There are two duct takeoffs in the charging aisle roof, one centered above each furnace. A damper is provided in each takeoff to open or close it as necessary. During hot metal charging and furnace deslagging the damper is opened to maximize the evacuation rate above the affected furnace.

Total air flow capacity for the partial building evacuation-hot metal handling secondary emissions system is 189 m^3/s (400,000 acfm) at 135° C (275° F). Flow is divided between partial building evacuation and hot metal handling, with 130 m^3/s (275,000 acfm) allotted to the roof ventilation system and 59 m^3/s (125,000 acfm) to the hot metal handling station. The available system pressure drop is 38 cm (15 in.) water column and gas cleaning is provided by a baghouse.[25]

Roof monitor visible emissions observations were made at this plant during May 1980.[26] These measurements were analyzed on the same basis as the Kaiser Steel data; i.e., 6-minute average opacities were calculated according to Method 9 procedures and the number of excursions equal to or greater than 20-percent opacity was determined. Table 10 presents the

TABLE 10. INLAND STEEL, EAST CHICAGO, INDIANA[26]

Date/	Cumulative percent of 6-minute averages less than or equal to given opacity										Number of individual observations
opacity	0	5	10	15	20	25	30	35	40	45	
5/12/80	44.1	79.2	89.6	98.8	100						479
5/13/80	83.6	100									1,273
5/14/80	40.0	88.4	100								1,504
5/15/80	22.2	66.2	83.6	89.6	94.7	97.3	98.4	98.9	99.9	100	1,46[illegible]
5/16/80	97.2	100									

6-minute average opacities for 5 days and Table 8 presents the average number of excursions per cycle segment for six production cycles.

The data in Table 10 show that on 3 of the 5 days the 6-minute average opacities were as good as those observed during the Kaiser Steel tests. On 1 of the remaining 2 days there were several readings in the 15- to 20-percent range, but none over 20 percent. On May 15, 6-minute averages in the 35- to 40-percent range were observed. No correlation was found between these high readings and events which transpired in the shop on that day.

Modified Primary Hoods

Bethlehem Steel, Bethlehem, Pennsylvania--

This BOF shop contains two 272-Mg (300-ton) furnaces equipped with open hoods ducted to an ESP. Each furnace is partially enclosed by side walls, with no enclosure on the charging or tapping sides. The only modification to the primary hood system is an awning-like structure constructed on the tapping side between the side enclosures that extends toward the teeming aisle. This awning acts like a flanged extension that helps direct tapping fumes into the primary hood.

During hot metal charging operations the gas evacuation rate for the primary hood is 236 m^3/s (500,000 acfm) at about 82° C (180° F).[23] The initial portion of the hot metal charge is performed with the furnace mouth tipped only partially out from under the hood. As the charge nears completion the furnace is tipped further, bringing the entire mouth out from under the hood. Fume escape is worst at the end of the charge. During the oxygen blow the primary hood evacuation rate is increased to 353 m^3/s (750,000 acfm) at a temperature of 210° C (420° F). When the vessel is turned down for tapping or other reasons the evacuation rate is reduced to the same level as for charging.[27 28]

TABLE 11. BETHLEHEM STEEL, BETHLEHEM, PENNSYLVANIA[29]

Date/ opacity	Cumulative percent of 6-minute averages less than or equal to given opacity 0	5	Number of individual observations
6/23/80	80.6	100	1,413
6/24/80	93.9	100	1,920
6/25/80	96.3	100	1,920
6/26/80	81.4	100	1,811

Roof monitor visible emissions observations were performed at this plant in June 1980.[29] Table 11 presents the results analyzed according to EPA Method 9, i.e., 6-minute average opacities based on observations made every 15 seconds. The table shows that no 6-minute average opacity exceeded 5 percent on the 4 test days.

Table 8 presents the data analyzed on the basis of the average number of individual opacity observations equal to or exceeding 20-percent opacity for eleven production cycles. The data are broken down into segments of the production cycle.

A significant portion of performance achieved at the Bethlehem plant must be attributed to good operating practice and skillful crane and furnace maneuvering. However, techniques employed at Bethlehem are not applicable to BOF shops with closed hoods that have insufficient draft for good secondary emissions capture.

Republic Steel, Gadsden, Alabama--

This BOF shop contains two 136-Mg (150-ton) furnace vessels with open hood primary gas-cleaning facilities. The secondary emission control system consists of Gaw dampers installed under the face of the primary hood of each furnace. During hot metal charging the Gaw damper closes off about 50 percent of the primary hood face area. Increased gas velocity at the front of the hood face improves capture efficiency of the primary hood during charging operations. The damper does not serve a similar function during tapping. The gas evacuation rate during hot metal charging is about 283 m^3/s (600,000 acfm) at a temperature of about 77° C (170° F). A reduced evacuation rate, about 165 m^3/s (350,000 at 77° C), is used during tapping, deslagging, and other turndowns.[30]

Visible emissions data were gathered at this plant in August 1979.[29] Roof monitor opacities were read during 42 furnace production cycles. These data were analyzed on the same basis as previously described.

TABLE 12. REPUBLIC STEEL, GADSDEN, ALABAMA[30]

Date/ opacity	Cumulative percent of 6-minute averages less than or equal to given opacity										Number of individual observations
	0	5	10	15	20	25	30	35	40	45	
8/20/79	60.5	94.4	97.2	98.2	99.1	100					1,992
8/21/79	52.6	90.0	96.2	98.3	99.5	99.7	100				2,002
8/22/79	40.9	84.7	90.0	95.1	97.9	98.8	98.9	99.1	99.2	100	2.344
8/23/79	8.9	94.3	97.1	99.3	100						1,860

The data in Table 12 show that 6-minute average opacities were not as low as those encountered at Kaiser Steel and Bethlehem Steel. However, the data analysis presented in Table 8 shows that the main problem with emissions occurred during the oxygen blow rather than during hot metal charging, turndown, or tapping. Process observations made during the tests indicate that these emissions were due to leaks through the oxygen lance hole, leaks in the primary hood, and a primary system gas evacuation rate lower (by 10 percent) for one furnace than the other.[30] The referenced report concludes that the Gaw damper effectively controlled hot metal charging emissions.

Performance Analysis

The performance of secondary emission control systems varies greatly between shops and very often, for any single system, varies on a day-to-day basis and sometimes on a heat-to-heat basis. The most consistent performance was seen at Bethlehem Steel, Bethlehem, Pennsylvania, where during 4 days of testing no 6-minute average opacity exceeded 5 percent (Table 7). In comparison, performance of the system at Republic Steel's South Chicago Q-BOP shop was not as good. On the best test day (6/20/79) approximately 4 percent of the 6-minute average opacities exceeded 5 percent while on the worst day (6/5/80) over 20 percent of the averages exceeded 5 percent (Table 9) with the highest exceeding 40 percent. The Kaiser system is analogous to the Republic Q-BOP system in that both have full furnace enclosures with local charging hoods. The Kaiser system which also has a tapping hood, has demonstrated superior performance with no 6-minute average opacity ever exceeding 15 percent and on the best day no 6-minute average exceeding 5 percent. This system's good performance is a result of the high evacuation rate and proper placement of the charging hood.

When comparing the Kaiser system to the Republic Q-BOP system, it should be kept in mind that tuyeres in bottom blown furnaces must be purged during all phases of the production cycle and that purge gases tend to propel emissions away from the mouth of the furnace making their capture by local hoods difficult. Such remedies as increasing the charging hood evacuation rate or installing a partial building evacuation system have not been tried in any domestic Q-BOP installation. Attention should be drawn to the fact that at one new Q-BOP installation in Japan the fugitive emission problem has apparently been solved through the use of both local hoods and a roof mounted ESP.[31]

The data displayed in Table 8 have been analyzed to determine the effectiveness of these systems during different segments of the production cycle. It is evident that the systems are not uniformly effective throughout the cycle. The Kaiser system allowed greater opacity emissions to escape during turndown than during charging or tapping. The Inland system, however, allowed more emissions during charging than during turndown or tapping. Inland's high opacity readings during oxygen blow have not been accounted for although it seems unlikely that they were due to any deficiencies in the secondary emission control system. A similar situation existed at the Republic Steel, Gadsden, plant, with the exception that high opacity readings during the oxygen blow were attributed to leaks in the primary system.[31]

During the 1980 test at Republic Steel, South Chicago,[25] there were no great differences in the number of opacity observations 20 percent or greater during charging, turndown, or tapping.[25] During the 1979 test, however, tapping created the greatest number of high readings.[24]

In general, the secondary emission control systems discussed above are capable of maintaining roof monitor opacities below 20 percent, with some exception for bottom blown furnaces. The effectiveness of secondary emission control systems is not uniform from one shop to another, and may not be uniform from one heat to another within a given shop.

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INVESTIGATION OF OPACITY AND PARTICULATE MASS CONCENTRATIONS FROM HOT METAL OPERATIONS

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ABSTRACT

The objective of this study was the investigation of possible relationships between plume opacity, mass concentration, and sub-10-μm mass concentration for three hot metal processes. Size distribution data from a blast furnace casthouse, BOF shop, and hot metal desulfurization were used to compute mass light extinction coefficients. A wide range of materials (iron oxide, carbon, and glass) were assumed to model the emissions. The results suggest that opacity-to-mass concentration should be insensitive to composition, and a good correlation of mass-to-plume opacity is expected. The emissions studied were of similar optical activity as those reported in the literature in other industries. The results of the analysis also imply that the sub-10-μm particles should be well correlated to mass.

It is recommended that future field tests to measure particle size distribution should include instrumental measurements of opacity. Thus, opacity, mass concentration, and sub-10-μm particle concentration could be subjected to a correlation analysis. In addition, the refractive index and particle density of particulate material should be measured on bulk material to aid in explanation of the test results.

INTRODUCTION

OBJECTIVES

The interrelationship of various emission limits for metal casting or pouring is of considerable importance in the determination of how to best regulate emissions. The purpose of this paper is to compare opacity, total thoracic particulate concentrations (particles with aerodynamic diameters less than 10 μm), and mass emissions. The present work is not intended to be definitive but indicative of the possibilities in emission data interpretation.

BACKGROUND

Opacity limitations are of considerable value in regulating the iron and steel industry. In particular, fugitive emissions common in iron and steel processes cannot easily be quantified in any other way.

Recently, test data were acquired and analyzed for emissions from certain processes involving operations with hot metal. The data included, in addition to process parameters, particle size distributions measured by cyclones and cascade impactors. A new computer program, which was recently written for the TRS-80™ microcomputer by Cowen, Ensor, and Sparks (1981) to allow computation of opacity from emission aerosol properties, facilitated the analysis.

THEORY

OPACITY AND TRANSMITTANCE

Opacity and transmittance are interrelated by the following equation:

$$Op = 100\ (1 - T) \tag{1}$$

where Op is the opacity (percent) and T is the fractional transmittance. The Beer-Lambert law relates transmittance to intensive properties of an emission aerosol:

$$T = \exp\ (-\ bL) \tag{2}$$

where b is the extinction coefficient (1/length) and L is the distance the light travels. In the present case, L is the diameter of the stack or plume.

The quantity of interest is the mass concentration, M, at actual conditions of temperature, pressure, and moisture. Equation 2 can be rewritten to include mass concentration:

$$T = \exp\ [-\ (b/M)\ M\ L]. \tag{3}$$

The ratio of extinction coefficient to mass concentration, $S_m = b/M$, is widely used in light transmission studies. It has also been called the mass extinction coefficient. Ensor and Pilat (1971) used the symbol "Sp." Conner, Knapp, and Nader (1979) termed it the quantity "A." In the present study, we will use "S_m." In computational work it is advantageous to work with aerosol volume concentration rather than mass concentration. The theoretical calculations, if performed with aerosol volume concentration for a given particle refractive index, can be scaled to any particle specific gravity.

The parameters based on specific aerosol volume are:

$$S_v = b/M\ \rho \tag{4}$$

where ρ is the specific gravity or density of the particulate matter. Ensor and Pilat (1971) defined a parameter "K" which is the reciprocal of S_v. The parameter K is very useful in relating mass to opacity (the current study is involved in relating opacity to an observed mass concentration). The equation using K to relate mass concentration to opacity is:

$$M = - \ln [(100 - Op)/100] K\rho/L. \quad (5)$$

In comparison to Equation 5, the equation relating opacity to mass concentration is:

$$Op = 100 [1 - \exp (- S_m M L)]. \quad (6)$$

Equation 6 will be used in the present study.

The effort in this study was directed at computing S_m as a parameter to characterize the emission. S_m is a qualitative measure of the "optical activity" of the emission and indicates the mass concentration required to meet an opacity limitation. The principle data reported from the field test were particle size distribution determined by cascade impactors. The other data required to compute S_m directly, such as opacity measured by a transmissometer, were not taken.

The extinction coefficient, b, from Equation 3, is computed by integrating over the size distribution using the Mie equations describing the interaction of electromagnetic radiation with dielectric spheres. The mass concentration, M, is computed by integrating the aerosol volume over size distribution and multiplying by particle density. The computational approach is described by Cowen, Ensor, and Sparks (1981).

APPLICATION TO A METAL FUME

QUALITATIVE DESCRIPTION OF THE EMISSIONS

The emissions resulting from the pouring of hot metal are a complex mixture of materials. The bulk of these materials is probably iron oxide. The remainder of the materials could be kish (a carbonaceous material), vaporized refractory material, or dust entrained by the hooding system. An additional complication in determining this mixture is the possible change of the emission properties during the process cycle, Nicola (1979). Cascade impactor samples have been reported (Gronberg, Piper, and Reicher 1981) for casthouse emissions to appear reddish in the lower stages and blackish in the large particle stages. A similar observation was reported by PEDCo (1981) for BOF shop emissions. The red material could be iron oxide in the hematite form. The black material could be iron oxide in magnetite form, or graphitic carbon. Thus, the evaluation of the mass-to-opacity relationship with various materials is an important part of the present study.

PHYSICAL PROPERTIES

The rather limited information available on particle properties of emissions from operations involving hot metal dictated a survey of a handbook for refractive index and specific gravity. The possible range in refractive index (transparent, 1.55, to absorbing, 3-1i) and specific gravity (1 to 5.3 g/cm^3) is quite large. Thus, one of the objectives of the analysis was to determine the sensitivity of the computed S_m to refractive and particle density.

DEVELOPMENT OF CASE STUDIES

The case studies were selected using a combination of measured particle size distributions and realistic physical properties. The following materials were assumed:

1. Iron oxide.
2. Graphitic carbon.
3. Glass.

The particle size distribution case studies were:

1. Blast furnace casthouse emissions during casting.
2. Blast furnace casthouse emissions between casts.
3. BOF shop emissions.
4. Hot metal desulfurization.

The blast furnace casthouse emission particle size distributions were reported by Gronberg et al. (1981) from tests conducted at DOFASCO in Hamilton, Ontario. The tests were made in the total building evacuation control system at the inlet of the baghouse. The emissions should be reasonably representative of uncontrolled emissions from the process.

The BOF emission particle size distributions were reported by PEDCo (1981) from tests conducted at the Armco Steel No. 16 basic oxygen furnace at Middletown, Ohio. The tests were done in the stack of the emission control system downstream of a high-energy venturi scrubber. The BOF is top-blown with a closed hood for emission control. Tests were conducted only during oxygen blowing.

The hot metal desulfurization emission particle size distributions were reported by Pope and Steiner (1980) from tests conducted at Kaiser Steel, Fontana, California. Predetermined amounts of calcium carbide and calcium carbonate were blown through a lance with nitrogen at 30 to 40 psi into a torpedo car containing hot metal. Emissions escaping the stopper around the lance were captured by a hood and ducted to a baghouse. Tests were conducted at both the inlet and outlet of the baghouse. Only the inlet particle size distributions were used in the present analysis.

Thus, a total of 12 different computer simulations were conducted because three different materials were modeled for four different size distributions.

PARTICLE SIZE DISTRIBUTION

The particle size distributions measured by various EPA contractors were used in this study. From a general examination of the data, all of the distributions are not lognormal. Therefore, an incremental integration of the size distributions was conducted. The program used, called HISTOGRM/BAS, is described in detail by Cowen, Ensor, and Sparks (1981).

The reports used for the source of the size distribution data all are in draft form and should be considered preliminary.

RESULTS

EXTINCTION COEFFICIENT TO MASS CONCENTRATION FOR EACH PROCESS

The results of the computations for each particle property case and process are reported in Table 1. A surprising result for each process is the relative insensitivity of the calculation to the particle properties. (Graphitic carbon yields the highest S_m.) In addition, all the hot metal operations investigated have similar S_m's.

The insensitivity of calculated opacity to refractive index and density is explained by the shape of the particle size distributions emitted from these processes. The size distributions are larger than 1 μm aerodynamic diameter and very polydisperse. Thus, the extinction coefficient is averaged over a wide range of particle diameters resulting in a value of S_m insensitive to both composition and mean diameter fluctuations.

The opacity-to-mass concentration relationship should also be consistent from the modified Beer-Lambert law in Equation 6. In other words, opacity should be well correlated to mass concentration. A transmissometer would provide a reasonably accurate measure of mass concentration.

EXTINCTION COEFFICIENT AS A FUNCTION OF PARTICLE DIAMETER

Additional examination of the particle size distribution effects is shown in Figures 1 through 4. The cumulative percentage "less than" is plotted as a function of aerodynamic particle diameter for each process. In all cases the size distribution is very broad, as pointed out in the previous section.

The BOF emission appears to be bimodal. One distribution is less than 2 μm, while the other is larger than 10 μm. The BOF size distributions were the only case determined downstream of a control device (high-energy venturi scrubber). Thus, the bimodal nature of the size distribution may be due to the scrubber and not the particulate formation process. The high sub-2-μm particle concentrations may results from low efficiency of the scrubber in that particle size region, while the large particles may result from entrainment from the scrubber. However, the reported test results were inadequate to explain the observed distribution.

A significant observation is the extinction coefficient contribution by the material less than 10 μm in all processes. One obvious implication is control of opacity will require control of sub-10-μm particles (a restatement of common knowledge). Opacity is also a good indicator of sub-10-μm particle concentration.

Each case of assumed particle properties was plotted for each process. As shown in the figures, the emission properties do not affect the outcome to any great extent.

COMPOSITE EMISSION PROPERTIES

The emissions for these processes appear to be complex mixtures of compounds and a realistic simulation should consider a combination of the case study materials. For the purpose of comparison to other industries, a hypothetical mixture of components was used to compute an average S_m for the process shown in Table 2. It is understood that in reality the mixture of components may change during process cycles and may be substantially different than assumed here. In a very detailed study, the composition of the emissions would need to be carefully characterized. However, for the size distribution case studies investigated in this paper, the exact proportions are not critical.

COMPARISON TO OTHER INDUSTRIES

The literature was reviewed for opacity-to-mass data for other industries. These data are reported in Table 3. Note that the larger the S_m, the greater the resulting opacity for a given particle mass concentration or the greater the optical activity. One interesting result is that emissions from hot metal processes are not exceedingly optically active. Although pulverized coal-fired utility boiler emissions have about one-half the optical activity as hot metal processes, other industries, such as Portland cement manufacturers, have similar optical activity.

OPTICAL ACTIVITY OF TOTAL THORACIC PARTICLES

The analysis also suggests an important possibility for relating total thoracic particle concentrations and plume opacity. As demonstrated by the present theoretical calculations, the extinction coefficient results almost entirely from the total thoracic particles (sub-10 μm diameter). This suggests two possibilities:

1. Plume opacity would be highly correlated with the total thoracic particulate concentration. The correlation would be even better than that found for total mass concentration measured with EPA Method 5. This idea is analogous to results reported by Charlson et al. (1978) for visibility in the atmosphere. The correlation of visibility to sub-2.5-μm particle mass was observed to be much higher ($r = 0.82$ to 0.95) than to total mass concentration ($r = 0.3$ to 0.92). A total thoracic S_m (S_{mt}) is defined as the ratio of the extinction coefficient to the total thoracic mass concentration.
2. S_{mt}'s might be quite similar in magnitude for a wide range of industrial processes. The basis of this theory is that if only a narrow range of particle size (sub-10 μm) is considered and particle refractive index and density are secondary factors, the mass extinction coefficient would be relatively insensitive to the process.

These ideas are evaluated in Table 4. S_{mt} was computed by dividing S_m by the fraction of particles less than 10 μm aerodynamic diameter. The correlation of opacity to total thoracic mass concentration could not be directly tested by the rather limited nature of the data for the hot metal processes. (The opacity was not instrumentally measured, for example.) The potential of good correlation of the total thoracic mass concentration to opacity is suggested by some of the literature power plant data because the range of S_{mt}'s is smaller than S_m for the same source tests.

The contention that the S_{mt}'s for industrial emissions should be similar is borne out to some degree by the interindustrial comparison. The range of the S_{mt}'s is from 0.4 to 4 m^2/g. A systematic rereduction of the literature data combined with the objectives of determining the S_{mt}'s for various industries might narrow the range of values. At a minimum, the range of S_{mt}'s for each industry could be established in addition to determination of the correlation of opacity to total thoracic mass concentration.

In general, Table 4 demonstrates that these concepts have merit; however, insufficient data exist to develop firm conclusions.

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

Evaluation of the emissions expected for three hot metal processes in four test cases revealed that optical activity is fairly insensitive to the properties of the particles studied--iron oxide, carbon, and glass. Of these three materials, carbon was consistently the most optically active. Although the optical properties of the processes were quite similar, the BOF shop had the greatest optical activity (largest S_m). The insensitivity of the computed results to the particle properties is due to the averaging by the very polydisperse sized emissions of the extinction coefficient over a wide range of particle sizes.

In all cases the sub-10-μm particles were responsible for the light extinction. This observation suggests the hypothesis that various industries may have similar magnitudes of the total thoracic particulate S_{mt} (the extinction coefficient divided by the mass concentration of particles less than 10 μm aerodynamic diameter). It is also believed that opacity should be well correlated with total thoracic particulate concentration. However, the existing data base is too limited to prove the concept.

Comparisons of the computed S_m's and literature S_m's from other industries indicated similar magnitudes. Portland cement emission optical activity was almost identical to the computed results for hot metal activities. Pulverized coal-fired utility boiler emissions had about one-half the optical activity as the studied processes. However, comparisons of opacity from these two industries should consider the effects of stack diameter. The utility industry, with larger stacks than the iron and steel industry, may have similar opacity-to-mass concentration relationships.

RECOMMENDATIONS

Future test programs for particle size dependent emission factors should consider the use of optical transmissometers to measure opacity directly over a known pathlength. The opacity-to-mass relationships suggested by the computations in this paper should be verified experimentally. The light scattering computations described in this paper could be used to provide quality control as well as investigating the ramifications of the data.

Additional laboratory work should be conducted on the collected emissions from the hot metal processes to determine the particle physical properties. In particular, the particle density and the refractive index should be measured. The particles may have to be sorted into various particle populations as part of the investigation.

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TABLE 1. CALCULATED MASS EXTINCTION COEFFICIENT S_m (m^2/g)

Material:	Iron oxide*	Graphitic carbon**	Glass**
Refractive index:	3.0-1.0i	1.96-0.66i	1.55
Density (g/cm^3):	5.3	2.0	2.4
Process:			
Blast furnace casthouse			
During casts	0.926	1.68	1.06
Between casts	0.629	1.11	0.766
BOF shop	1.87	3.74	1.67
Hot metal desulfurization	0.681	1.31	0.942

Wavelength of light - 0.55.

* Refreactive index and density estimated from The Handbook of Chemistry and Physics (1959). The imaginary or absorbing part of the refractive index was assumed to be 1.0.

** The refractive index and density from Ensor and Pilat (1971).

TABLE 2. ESTIMATION OF COMPOSITE EMISSION MASS EXTINCTION COEFFICIENT S_m (m^2/g)

Component	Fraction of component	Blast Furnace Casthouse				BOF shop		Hot metal desulfurization	
		During casts		Between casts					
		Pure	Fraction	Pure	Fraction	Pure	Fraction	Pure	Fraction
Iron oxide	0.60	0.926	0.556	0.629	0.377	1.87	1.12	0.681	0.409
Graphitic carbon	0.35	1.68	0.585	1.11	0.390	3.74	1.31	1.31	0.459
Glass	0.05	1.06	0.053	0.766	0.0383	1.67	0.084	0.942	0.0471
Total			1.20		0.805		2.52		1.11

TABLE 3. COMPARISON OF THE CALCULATED MASS EXTINCTION COEFFICIENT TO OTHER SOURCES

Source	S_m (m^2/g)	Reference
Pulverized coal-fired boiler	0.30 to 0.49 0.78 0.58 0.4 to 0.92 0.1 to 0.5	Conner (1974) Ensor and Pilat (1971) Conner (1981) Ensor et al. (1979) Brennan and Dennis (1980)
Coal stoker smoke	6.1	Ensor and Pilat (1971)
Portland cement (wet process)	1.55	Conner et al. (1979)
Portland cement (dry process)	0.92	Conner et al. (1979)
Oil combustion	0.20 to 0.43	Conner at al. (1979)
Casthouse		
During casts	1.2	This study
Between casts	0.81	This study
BOF shop	2.5	This study
Hot metal desulfurization	1.11	This study

TABLE 4. ESTIMATION OF S_{mt}

Process	Total S_m (m^2/g)	Fraction less than 10 μm diameter	S_{mt} (m^2/g)	Reference
Pulverized coal-fired boiler	0.58	0.91	0.64	Conner (1981)
Portland Cement				
Wet process	1.55	0.85	1.82	Conner et al. (1979)
Dry process	0.92	0.75	1.23	Conner et al. (1979)
Oil-fired boiler	0.20 0.43	0.60 0.90	0.33 0.48	Conner et al. (1979)
Blast furnace casthouse				
During casts	1.2	0.53	2.2	This study
Between casts	0.8	0.39	2.1	This study
BOF shop	2.5	0.68	3.7	This study
Hot metal desulfurization	1.1	0.73	1.5	This study

$$S_{mt} = \frac{S_m}{\text{Fraction mass less than 10 μm}}$$

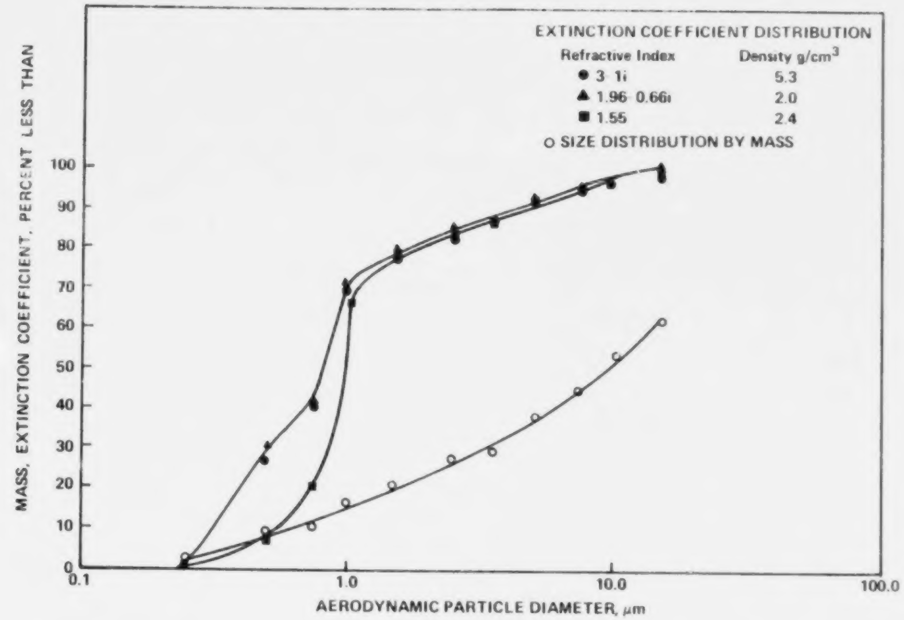

Figure 1. Cumulative percentage of mass and extinction coefficient for casthouse emissions during casts.

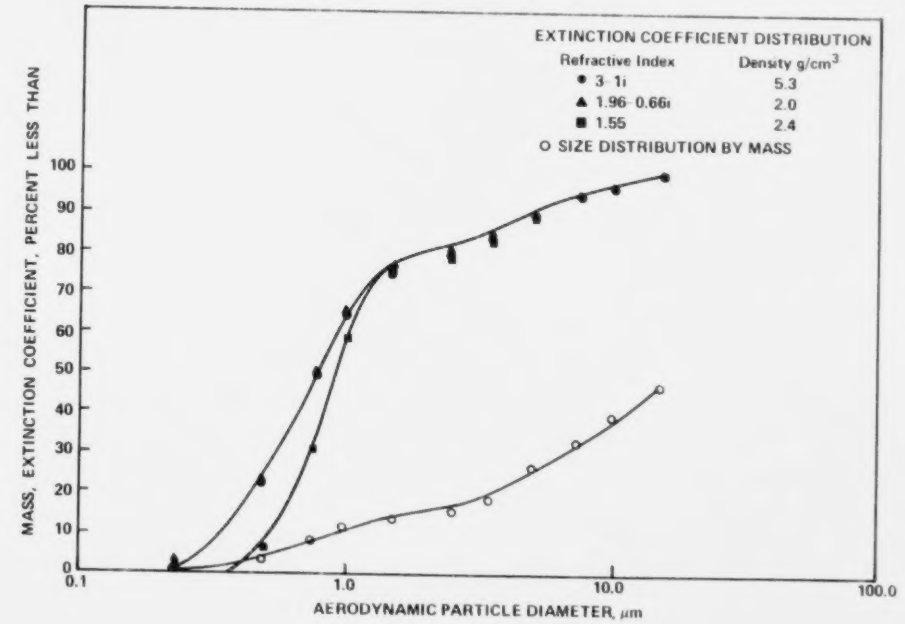

Figure 2. Cumulative percentage of mass and extinction coefficient for casthouse emission between casts.

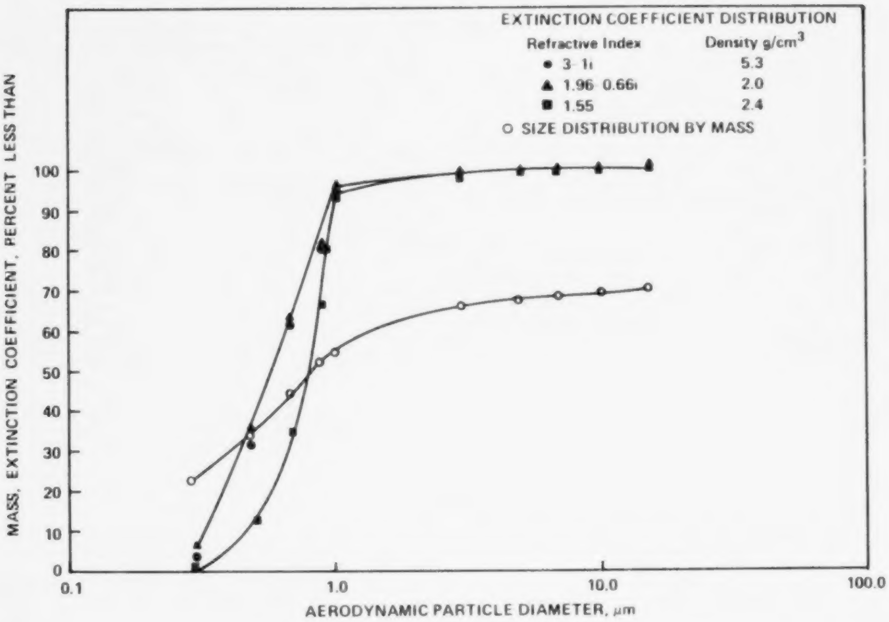

Figure 3. Cumulative percentage of mass and extinction coefficient for BOF shop emissions.

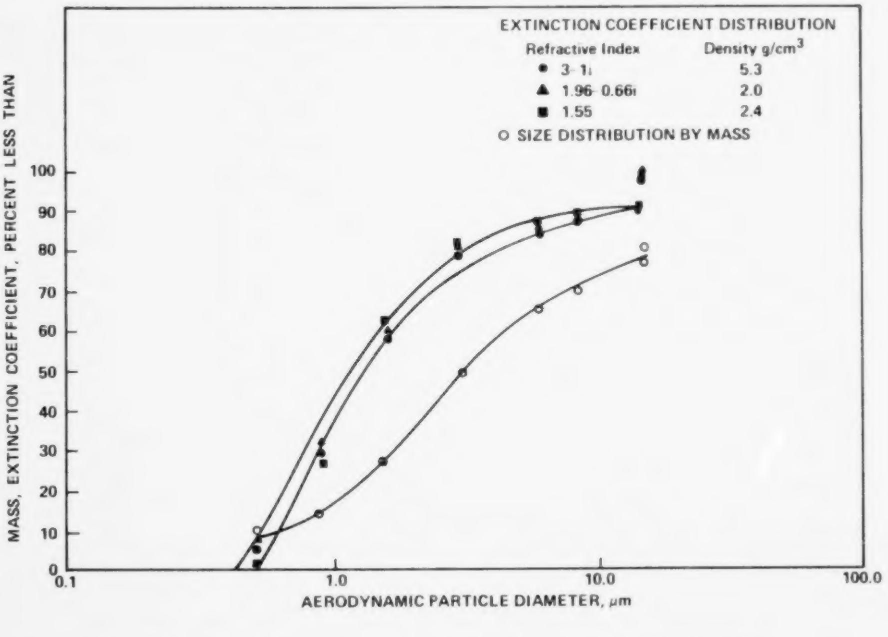

Figure 4. Cumulative percentage of mass and extinction coefficient for hot metal desulfurization emissions.

RETROFITTING EMISSION CONTROLS ON ELECTRIC FURNACES AT A STEEL MILL

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ABSTRACT

The body of information presented in this paper is directed to design engineers, electric arc furnace owners, and others who are interested in air pollution emission control technology. This paper presents the methodology and results of a two year project at the Knoxville Iron Company. An extensive field measurement program was conducted to quantify plume generation rates from two-30 ton electric arc furnaces melting scrap. Plume measurements were made for charging, tapping, and melting. Measurements were also made for tundish lancing and billet cutting. Maintenance and operational problems of the first generation side draft-hood and baghouse system were inventoried. Based on the source characterization and system performance, an integrated air pollution control system was designed and installed. Installed system capacity was 300,000 ACFM utilizing two shaker-type baghouses with flow switching and continuous limestone injection. Capital and installation costs are presented by major category. In addition, pertinent design parameters and system performance data are presented.

PRODUCTION FACILITIES

The shop has one 12 ft. diameter furnace rated at 12.5 MVA and one 12.5 ft. diameter furnace rated at 15 MVA. Both furnaces are floor mounted, and top charged with scrap bucket. Liquid steel is tapped into a ladle which is positioned in the tapping pit. Nominal weight of each tap is 30 tons, with approximate tap-to-tap times of 2 to 2½ hours. The melt shop operates continuously.

Charge materials consist of shredded automotive scrap, borings, turnings, and other miscellaneous scrap iron, lime, and ferroalloys. The product from the furnaces is low carbon steel used for reinforcing bar production. Oxygen lancing through the slag door is used for carbon content control.

Molten metal from each furnace is transferred by crane to the casting platform. Molten metal is withdrawn from the bottom of the ladle. It is split into three liquid streams by means of a refractory lined manifold (Tundish). If the openings in the bottom of the tundish become clogged or flow of the molten metal is not continuous, the tundish is removed from the casting machine. The openings are unclogged by blowing oxygen (tundish lancing) through them. A small diameter pipe with oxygen at 50 to 100 psi is used. The injected oxygen burns away the hot metal which has solidified in the bottom of the tundish. Each liquid stream is continuously cast into a 3" to 4" square strand. Each strand is automatically cut to a predetermined billet length. Cutting is performed with oxy-natural gas torches. The hot billets are transferred to a scrap preheater and are then stockpiled for future use in the rolling mill, where they are reheated and rolled into reinforcing bar.

HISTORICAL PERSPECTIVE

Air pollution control equipment was installed on Furnace No. 1 in 1972. The system consisted of an eight compartment shaker type pressure baghouse. Design flow was 128,700 ACFM @ 250° Fahrenheit with a gross air-to-cloth ratio of 3.25, and a net air-to-cloth ratio of 3.71. The fume collection system consisted of a 70" diameter duct connected to a 4' x 6' side draft hood mounted on the furnace. In addition a 70" duct was installed in the building roof above the furnace to collect fumes from charging and tapping.

In July 1975 a second furnace was installed and fitted with a similar emission control system. The system consisted of a ten compartment shaker type pressure baghouse. Design flow was 168,000 ACFM @ 250° Fahrenheit with a gross air-to-cloth ratio of 3.11 and a net air-to-cloth ratio of 3.46. A side draft hood and an 82" overhead duct were also installed. (See Figure 1.)

During the period of 1975 to 1977, various portions of the emission control system became inoperative. Chronic maintenance problems were experienced at the shaker mechanism, isolation dampers, overhead switching dampers, side draft hoods, bags, and dust handling systems. By 1977, the total system had degenerated to a state where it could not adequately control emissions despite major maintenance efforts. In 1977 the company was formally notified by the local regulatory agency that corrective measures would have to be instituted.

PHASE I. FEASIBILITY AND CONCEPTUAL DESIGN

The feasibility and conceptual design phase was started in September of 1977. Phase I consisted of two major areas, 1) Source characterization and 2) Existing baghouse system performance.

I. Source Characterization
    A. Furnace Operations
        1. Melting
        2. Tapping
        3. Charging
II. Existing Baghouse System Performance

Concerning source characterization, various methods were used to quantify plume generation rates.

MELT OPERATIONS

Pitot tube traverses were taken in the ductwork that services the side draft hoods. In addition, static pressures (draft) near the mouth of the hoods and fan amps in conjunction with total pressures across the fans were measured during normal melt operations. Visual observations as to the degree

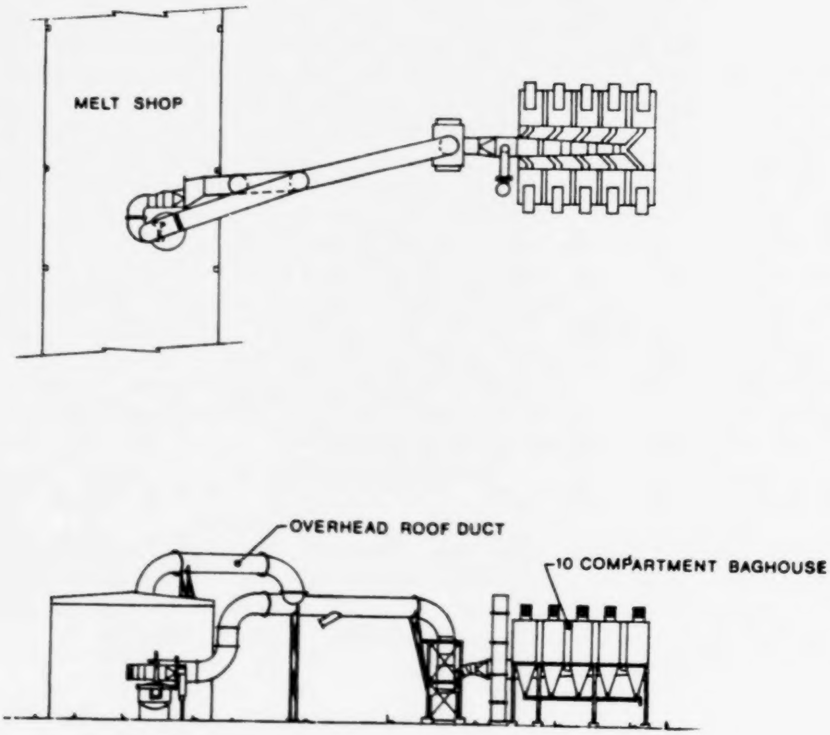
MELT SHOP
OVERHEAD ROOF DUCT
10 COMPARTMENT BAGHOUSE

FIGURE 1. OLD EMISSION CONTROL SYSTEM FURNACE NO.2

of capture during these measurements were also taken. From these data, the necessary flow to provide adequate capture at the side draft hoods was determined.

TAPPING/CHARGING AND TUNDISH LANCE OPERATIONS

The volumetric flow rate of the plume generated during the furnace tapping operation was measured by two methods. Method 1 consisted of timing the centerline ascent of the plume over a known distance in conjunction with the taking of a photograph. The photograph was subsequently analyzed to determine the entrainment angle and the cross sectional area, see Figure 2.

A recent investigation (Reference 1) of hot, buoyant plumes indicate that plumes generated from a point source rise and spread according to some definite physical relationships. It was found that unobstructed plumes of this nature spread at an angle of approximately 18° (entrainment angle) and that the average rise velocity for the total cross section is approximately 50% of the maximum rise velocity observed at the plume centerline or core. These relationships were used to calculate the volumetric flow rates. Method 2 consisted of allowing the plume to impact on the roof of the building, spread to the total width of the building and then be transported along the roof trusses by overhead drafts. The depth of the confined plume below the roof was observed to determine the cross sectional area and the total length of the plume was also observed. The above measurements yielded a total plume volume in cubic feet and the volumetric flow rate was calculated based on the measured time of plume generation.

TORCH CUTTING OPERATIONS

The volumetric flow rates above the three strand torch cutting operation were measured with a vane type anemometer. Velocity measurements were taken at 24 points approximately 5 ft. above the actual cutting location. Photographs and visual observations were made to determine the cross sectional area of the hot bouyant plume.

RESULTS OF SOURCE CHARACTERIZATION

Detailed results of the source characterizations are presented in Reference 2. Based on the results of the field measurements, the following design rates were determined:

1. Side Draft Hood ----------- 90,000 ACFM each
2. Charging/Tapping Hoods ---- 200,000 ACFM each
3. Tundish Lancing Hood ------ 110,000 ACFM
4. Torch Cutting ------------- 30,000 ACFM

EXISTING BAGHOUSE EVALUATION

A detailed analysis of the baghouse system was undertaken. The analyses consisted of:

1. Total system flow rates
2. Static pressure profiles throughout the entire system
3. Pressure drop across individual compartments
4. Review of maintenance records

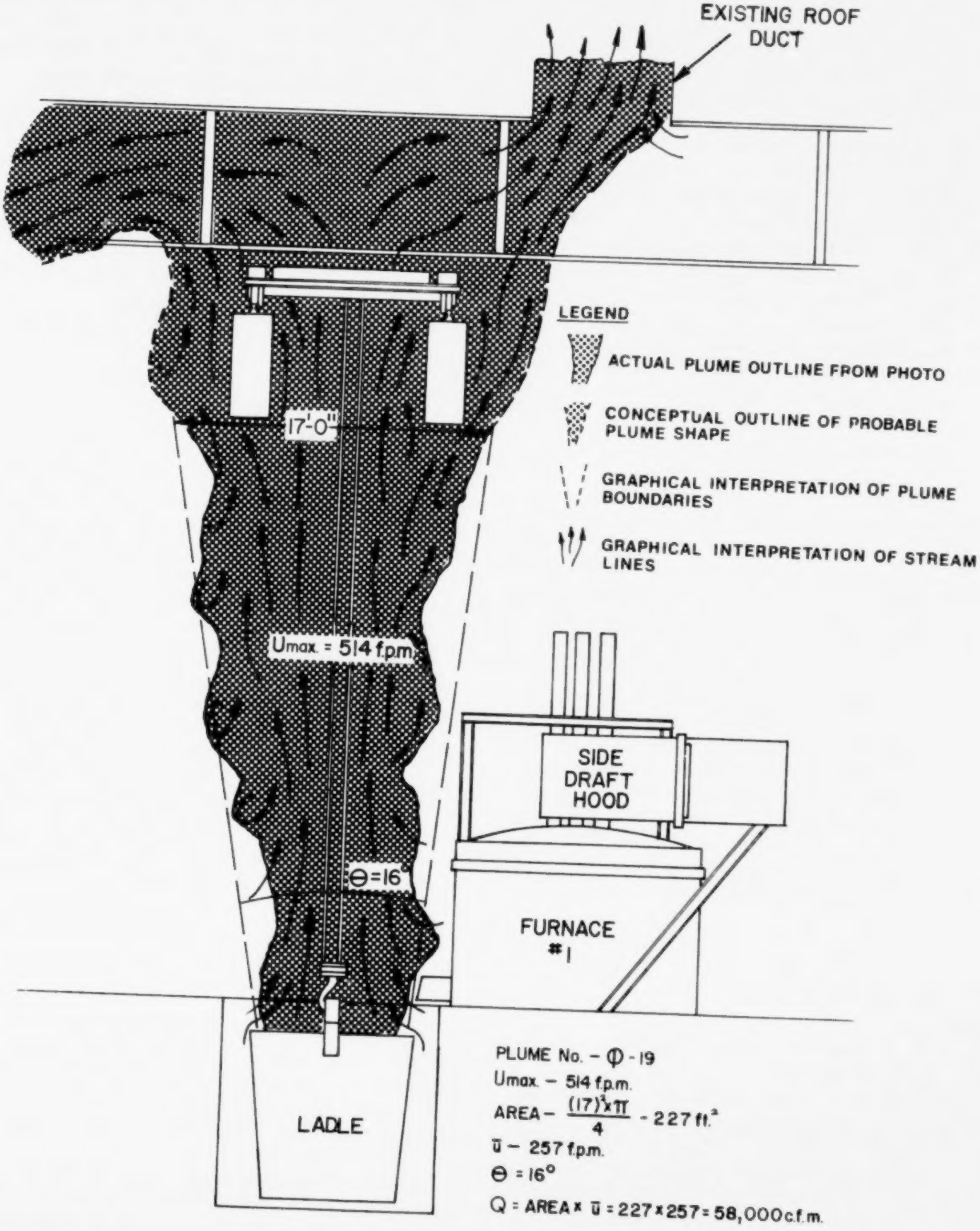
EXISTING ROOF DUCT
LEGEND
ACTUAL PLUME OUTLINE FROM PHOTO
CONCEPTUAL OUTLINE OF PROBABLE PLUME SHAPE
GRAPHICAL INTERPRETATION OF PLUME BOUNDARIES
GRAPHICAL INTERPRETATION OF STREAM LINES
17'-0"
Umax. = 514 f.p.m.
Θ=16°
SIDE DRAFT HOOD
FURNACE #1
LADLE
PLUME No. – Φ-19
Umax. – 514 f.p.m.
AREA – (17)²×π / 4 – 227 ft.²
ū – 257 f.p.m.
Θ = 16°
Q = AREA × ū = 227×257 = 58,000 c.f.m.

FIGURE 2. ILLUSTRATION OF TAPPING PLUME.

5. Extensive interviews with maintenance personnel
6. Inspection of failed parts

Based on field measurements, the dust collection system was operating at about one-half of its design capacity (i.e., ∿ 55,000 ACFM at baghouse #1 and ∿ 75,000 ACFM at baghouse #2). Pressure drop measurements showed from 13 to 14 inches pressure drop (back pressure) across each bag compartment. Air-to-cloth ratios were measured at 3.7 to 5.1:1 on functioning compartments. These conditions were detrimental to baghouse performance and expecially bag life. The bags did not last long at these high air;cloth ratios. Baghouse compartments which had recently been rebagged quickly blinded because of the high air-to-cloth ratios and heavy dust loadings. Total available static pressure across the fans was determined to be ∿ 15 inches (w.g.) at 150° Fahrenheit. Both baghouses were operating at the peak of the fan curves with 87-93 percent of the resistance in the system due to the filter bags. Normally, the system should have operated with 50-60% of the resistance due to the bags and 40-50% due to the ductwork resistance.

The primary reason for the reduced system performance was due to the number of bag compartments which were not functional due to old blinded bags. Bag blinding occurs when fine particulate matter fills the interstices of the fabric so completely that there are few remaining pathways for gases to travel through the fabric, hence the bags presented a high resistance to air flow. Bag blinding has been exaggerated by the "sticky" nature of the dust which was not easily removed from the bags.

The decline of the system performance was not tracked to any single cause, but rather a series of events. Of prime importance were isolation damper malfunctions and of secondary importance was fabric selection. The isolation dampers were equipped with small electric actuators which could not adequately open and close the dampers. The problem was exaggerated because the dampers were located on the dirty air side of the bags. The bags became heavily loaded with dust and overloaded the shaker mechanisms which failed repeatedly. Some early fabric selections had been toward rather heavy bags with poor cake release properties. It was impossible for the maintenance personnel to keep up with rebagging, repairing shaker mechanisms, and maintaining isolation dampers. Hopper bridging and maintenance on the lead section of the side draft hoods was also a continual problem. The large dampers which were designed to switch the flow from the side draft hoods to the overhead duct were inaccessible except by crane, and had become inoperable.

DETAILED DESIGN

TORCH CUT

Further investigation into the torch cut emission problem revealed that an oversized torch tip was being used. The torch manufacturers were contacted. They indicated that a smaller torch tip should be adequate. Aside from the physical size, the old torch tip used considerably more oxygen and gas. New torch tips were installed and tested. The new torch tips adequately cut the billets and visible emissions were virtually eliminated. In conjunction with the new torch tips it was also learned that operators had a tendency to set the oxygen regulator up to 140 psi. This was done when the body of a torch became misaligned, and rather than correcting misalignment, oxygen pressure was increased to compensate. Any over supply of oxygen again produced some visible emissions.

As a consequence, the oxygen regulators were locked at 100 psi. With these two minor corrections, a serious source of visible emissions was completely eliminated.

MODIFIED SYSTEM ARRANGEMENT

It was determined that if minor adjustments were made to the process schedule, the existing baghouse system had sufficient capacity to control emissions. Maximum fan capacity and flow switching would be required to maintain design volumes at each emission point.

Shown in Figure 3 is a plain view of the new system arrangement. Baghouse No. 1 was redesigned to handle 130,000 ACFM at 150° Fahrenheit, and baghouse No. 2 was redesigned to handle 160,000 ACFM at 150° Fahrenheit. In order to insure maximum flow rates, four additional compartments were added to each baghouse. This lowered the gross air-to-cloth ratio to 2.1 to 1. Compartments were added with minimal ductwork modifications.

The existing side draft hoods were judged to be quite adequate, except for the persistent maintenance problems associated with the water cooled section. A new inlet section was designed using 340 stainless ½" corrugated plate. The corrugated material was used to minimize stresses due to thermal expansion and contraction. The overhead roof ducts were judged to be totally inadequate, and a new overhead hood system was designed.

The new overhead hood system was designed in conjunction with the side draft hoods to provide the following design volumes.

Side Draft Hood------------------	80,000 CFM (adjustable)
Overhead Tapping/Charging -------	210,000 CFM
Tundish Lancing -----------------	130,000 CFM (On demand)

Process limitations were that only one furnace could be tapped or charged at a time, and tundish lancing only when both furnaces are under normal melt conditions. Flow distribution is accomplished by sensing static pressure on the side draft hood leg. The measured static pressure is maintained by a feed back loop connected to the modulating damper in the overhead hood system. In this manner, excess capacity from each baghouse (that which is in excess of 80,000 CFM) is used to control tapping/charging, or tundish lancing.

So that the design flows would be used most efficiently to capture emissions, new hoods were designed for above each furnace and the tundish area. Shown in Figure 4 is a drawing of the charging/tapping hoods. Each hood is internally partitioned, and appropriately dampered to direct the flow to the charging/or tapping area. Each hood has overall dimensions of 44' x 24' at the face. Each partitioned area is 32' x 24' at the face, which produces an average face velocity of 275 fpm. A flat flanged area, 5 ft. wide was installed around the perimeter of the hoods. The flange helps to increase the net effective area of the hoods. The hoods are located 37 ft. above the top of the ladle during tapping, and 30 ft. above the lip of each furnace. The tundish hood is 18' x 22' at the face, with an attached 5 ft. wide flange, and is located 15 feet above the tundish. The sides on all hoods have a minimum slope of 45° from horizontal. The upper portions of the hoods and ductwork were fabricated out of 10 gage mild steel, and the lower section utilized 20 gage corrugated sheeting.

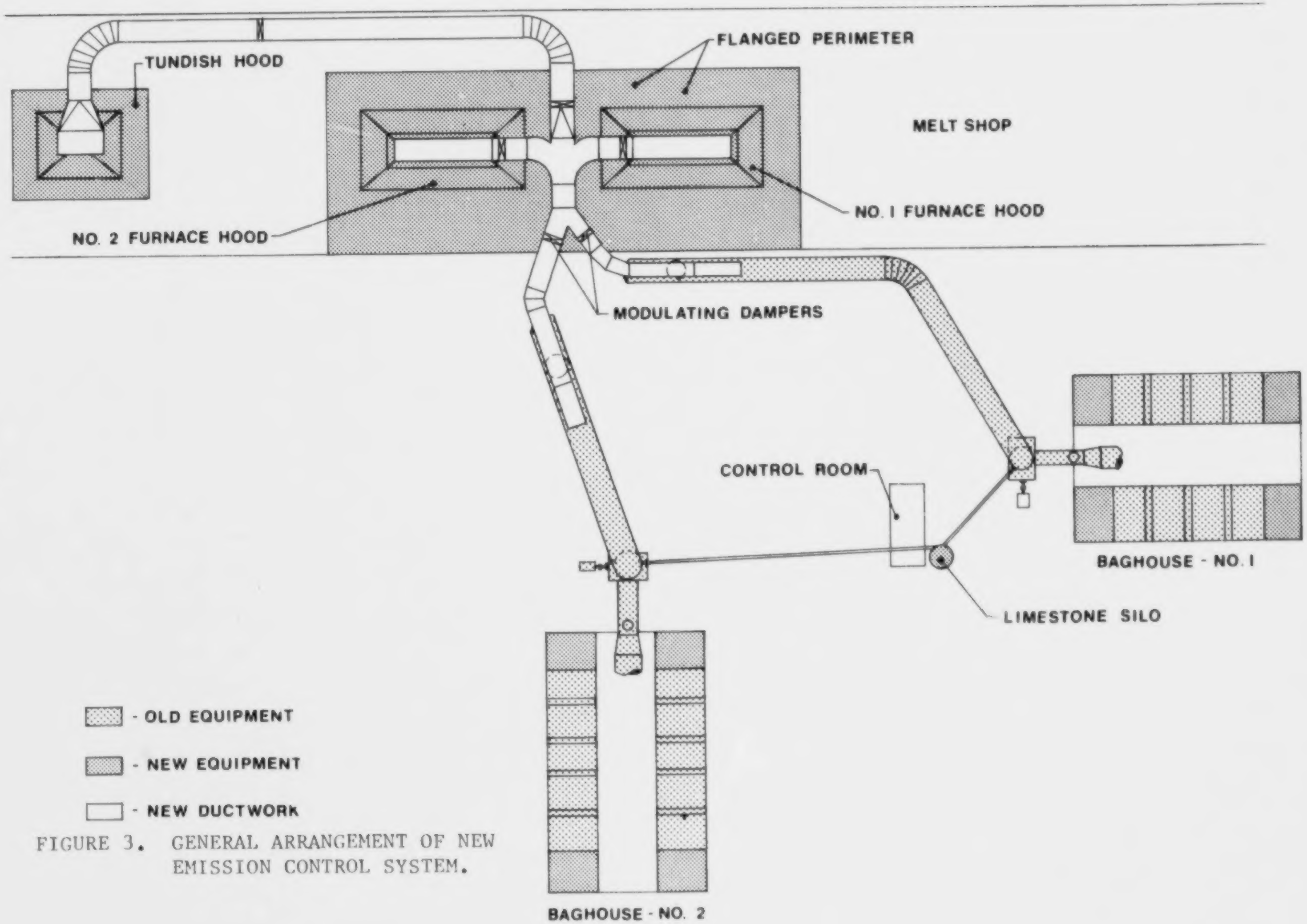
TUNDISH HOOD
FLANGED PERIMETER
MELT SHOP
NO. 2 FURNACE HOOD
NO. 1 FURNACE HOOD
MODULATING DAMPERS
CONTROL ROOM
BAGHOUSE - NO. 1
LIMESTONE SILO
BAGHOUSE - NO. 2
▨ - OLD EQUIPMENT
▨ - NEW EQUIPMENT
☐ - NEW DUCTWORK

FIGURE 3. GENERAL ARRANGEMENT OF NEW EMISSION CONTROL SYSTEM.

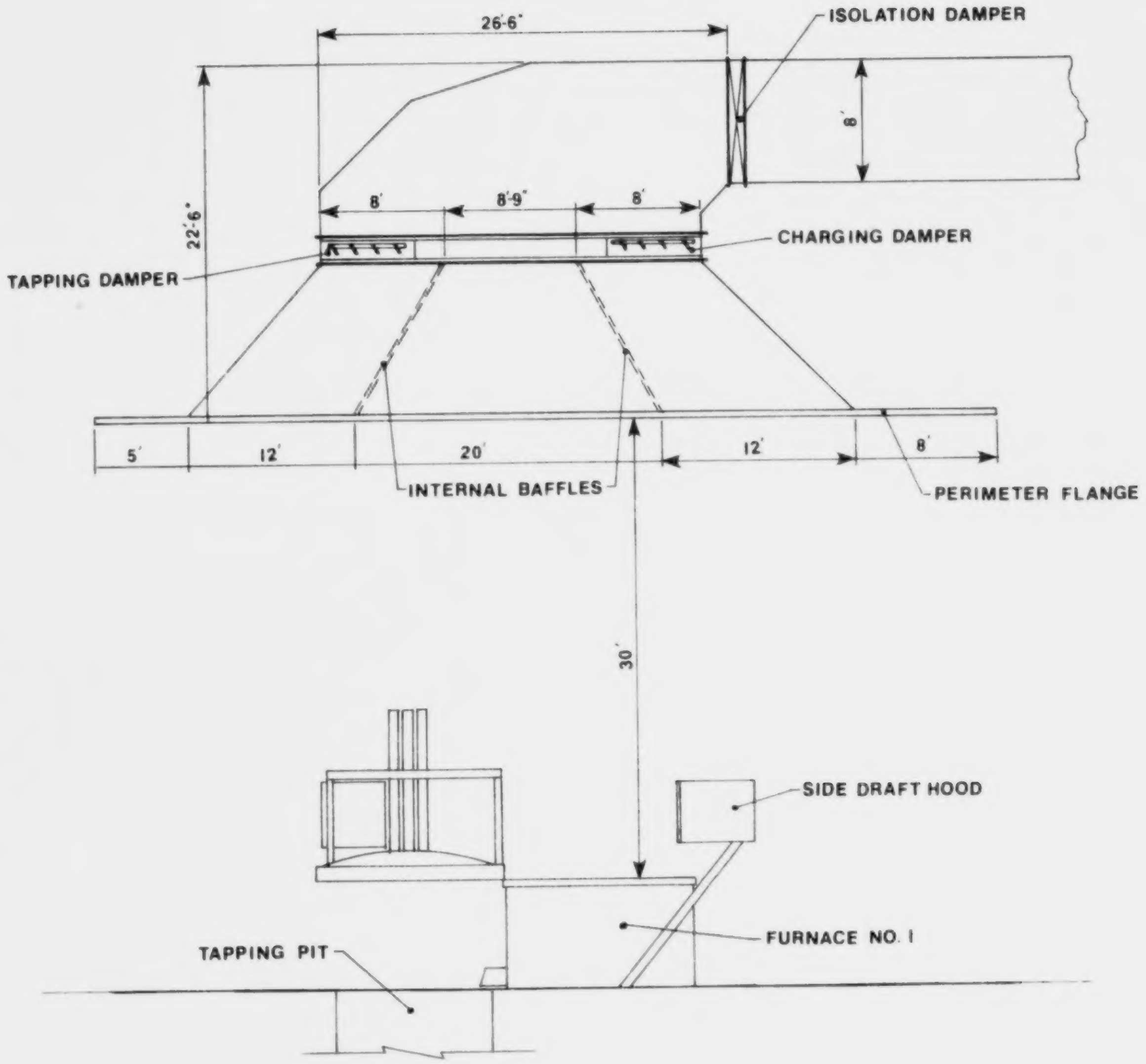
26'-6"
ISOLATION DAMPER
8'
22'-6"
8'
8'-9"
8'
CHARGING DAMPER
TAPPING DAMPER
5'
12'
20'
12'
8'
INTERNAL BAFFLES
PERIMETER FLANGE
30'
SIDE DRAFT HOOD
FURNACE NO. 1
TAPPING PIT

FIGURE 4. NEW OVERHEAD FURNACE HOOD

BAGHOUSE

In addition to the placement of four new compartments on each baghouse, extensive work was done on the old compartments. The bag material finally selected was a 5.7 oz/sq. yd. Nomex, with a smooth surface for good cake release. Although many arc furnace systems use polyester bags, it was felt that since this system had to operate at maximum capacity, the addition of cooling dilution air would have adversely affected the long term performance.

A detailed examination of all of the isolation dampers revealed that aside from dust build up on the seating surfaces, the dampers were operable. It became evident that the electric actuators were not adequate. For these reasons, new compressed air actuators were installed on all of the dampers. All dampers except the fan inlet dampers and the two overhead modulating dampers were retrofitted with pneumatic actuators.

A limestone injection system was also installed. The system consists of a 50 ton pressurized storage silo, connected to two variable speed feeders. Pulverized limestone is injected at a rate of 80 to 120 lbs/hr. to each baghouse. Feed rate is adjusted according to type of scrap being melted, with the higher rate corresponding to the melting of oily scrap. The limestone is used primarily to slow the process of bag blinding, and to aid in cake release. Also of prime importance is the fact that the limestone effectively changes the size distribution of the dust, and tends to build a more "porous cake", hence a lower pressure drop across the filter. The limestone lessens the phenomena of bleeding by extending the effective filtration depth. The limestone injection system is used to condition new bags. The injection system is completely automatic, and is refilled from a pressurized tank truck.

A centralized control room was built to house the compressed air system, motor control center, and control panel. Considerable effort went into the design of the control panel, which is shown in Figure 5. The main objective of the control panel design was to assist maintenance personnel in system operation, and to enable them to be able to detect short term malfunctions, and long term problems. Aside from the usual manditory control and monitor functions such as fan performance, and compartment cleaning, a series of other functions are monitored or controlled. Every damper in the system was equipped with a magnetic type position detector, and damper position is indicated on the panel with color coded display lights. Every individual compartment function is also monitored with indicator lights. Functions include shaker motors, rotary air-lock drive, screw conveyor motors, and shake and isolate time. Inlet gas temperature to each baghouse is monitored on strip chart recorders. The set point controllers and monitors for side draft hood static pressure are displayed in conjunction with modulating damper position. Miscellaneous functions such as limestone injection feeders, limestone silo fill conditions, and compressed air pressures are displayed. System pressure drop across each baghouse is also monitored and continuously recorded on strip charts. Shown in Figure 6 is an example of the trace from baghouse No.2. System pressure recording allows the operators to adjust cleaning cycle times to optimize equipment life. Pressure drop monitoring also allows the operators to spot long term problems if they arise. Most systems that do not record pressure drop only allow the operators to respond to short term acute problems. Hence, no potential to develop a long term maintenance program which is vital to successful baghouse operation.

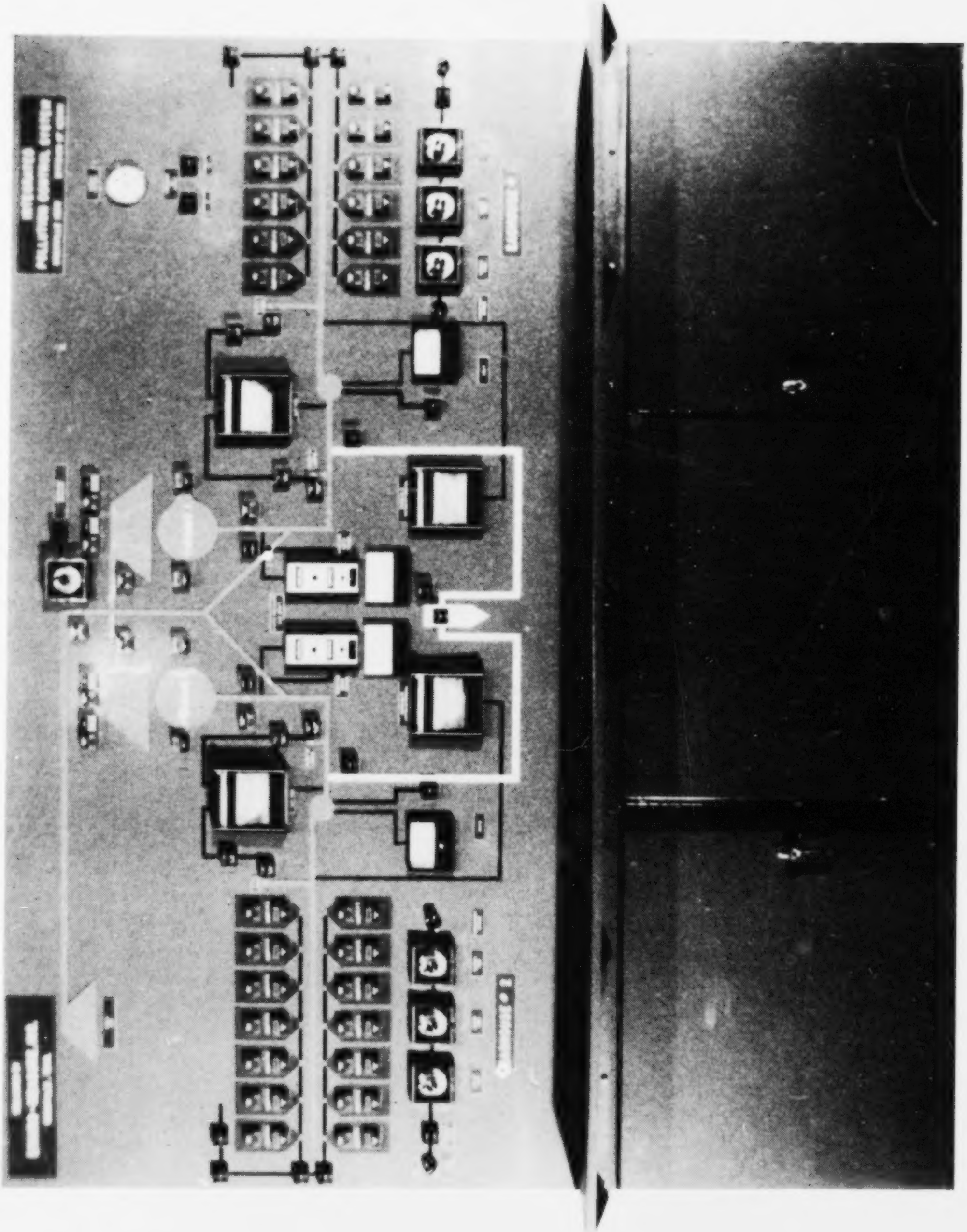

FIGURE 5. SYSTEM CONTROL PANEL

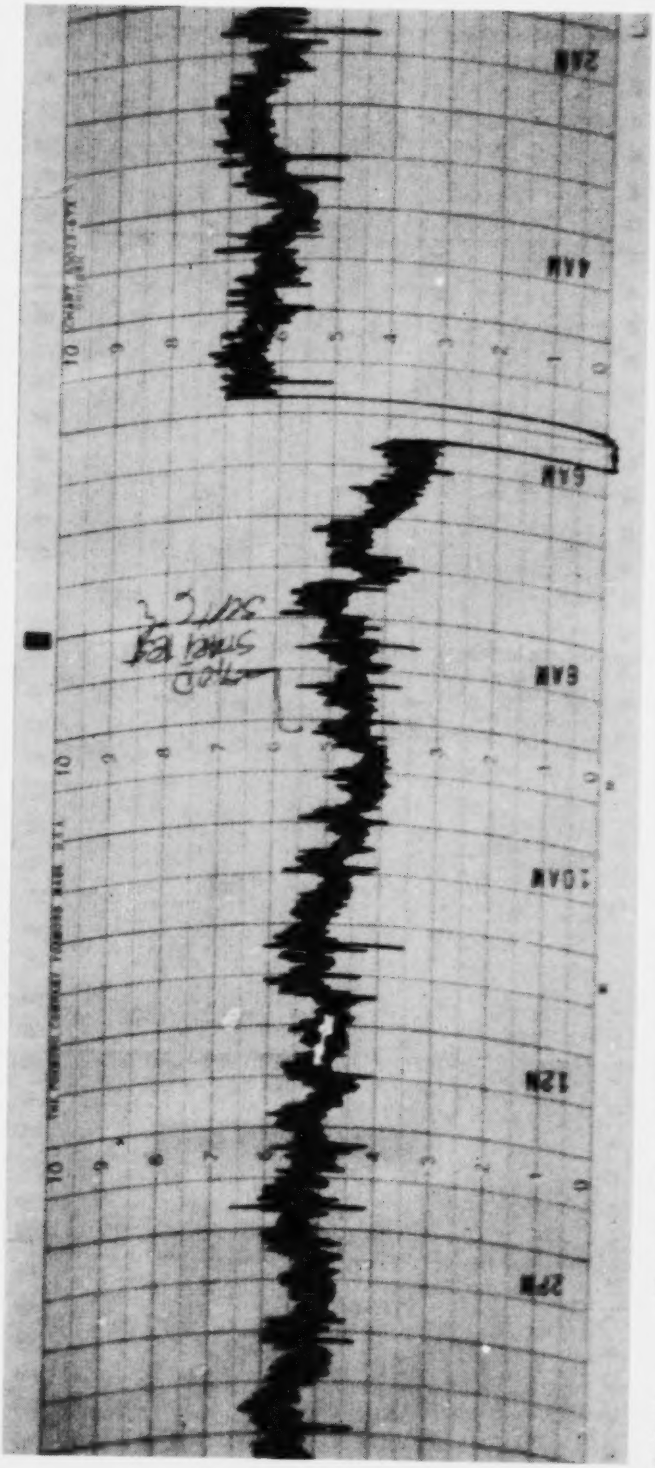

FIGURE 6. TYPICAL STRIP CHART RECORDING OF PRESSURE DROP ACROSS BAGHOUSE.

Extensive walkways were added so that every damper in the system could be easily serviced by maintenance personnel. The dust handling system was rebuilt. New rotary locks and screw conveyors were added. In addition, a common vented dust storage area for each baghouse was constructed. Pressure taps were installed on each compartment, and a panel of pressure gages was mounted in the control room. The entire system was completely rewired and painted.

SCHEDULING

Shown in Figure 7 is an aerial view of the completed project. Baghouse No. 1 is on the right, with the limestone storage silo, and the new control room is located between the two baghouses. The overhead ductwork and hoods are shown. The long duct run in the background is to the tundish area. The torch cut area is at the base of the tall stack.

Construction and installation of the system was begun in 1978 and completed in April 1979. Critical path method scheduling was employed and the project was completed on time. No production time was lost due to the installation. Two week long highly manpower intensive periods were employed to install critical equipment. These periods were scheduled to coincide with scheduled furnace maintenance periods. Work completed during these periods consisted of removing all old bags and placement of new bags, completely rebuilding shaker mechanisms, replaceing rotary locks and screw conveyors, and completing final electrical hook up. Work was completed by a 30 to 40 man crew. Upon completion of the installation, the system was started, and the new bags were conditioned for 16 hours with limestone dust.

The entire project had been cost estimated during the feasibility study period at approximately 1.2 million dollars. The project was completed within the budget allocation. Approximately 50% of the total budget was for materials, 40% for labor, and 10% for engineering and project management.

Performance and compliance tests have been done on the system. The results show that baghouse No. 1 is running at 99% of design capacity of 130,000 CFM and baghouse No. 2 is running at 116% of its design capacity of 160,000 CFM. Visible emission observations by the local inspectors have consistently shown that visible emissions from the mill have been eliminated. Outlet grain loadings averaged 0.003 gr/DSCF for six tests, and mass emission rates were 6.9 lbs/hr. total from both baghouses.

SYSTEM UPDATE

Since the completed installation in 1979, several system/operations modifications have been made. In September 1980, a scrap preheat system was installed. The scrap preheater is used to preheat approximately 70% of the charge material. Heat for the scrap preheater is supplied by the hot billets. The scrap is preheated to a sufficiently high temperature to drive off oil and rubber fumes. The exhaust gases from the scrap preheater are cooled and then pass through a knockout chamber and small filter section to remove condensed oil and rubber aerosols. The exhaust gases are then vented to baghouse No. 1. The reduced oil and rubber fumes from the furnace melting operations have decreased substantially the "stickiness" of the dust emissions to the baghouses. Because of this, it is now possible to operate the system without the limestone injection system.

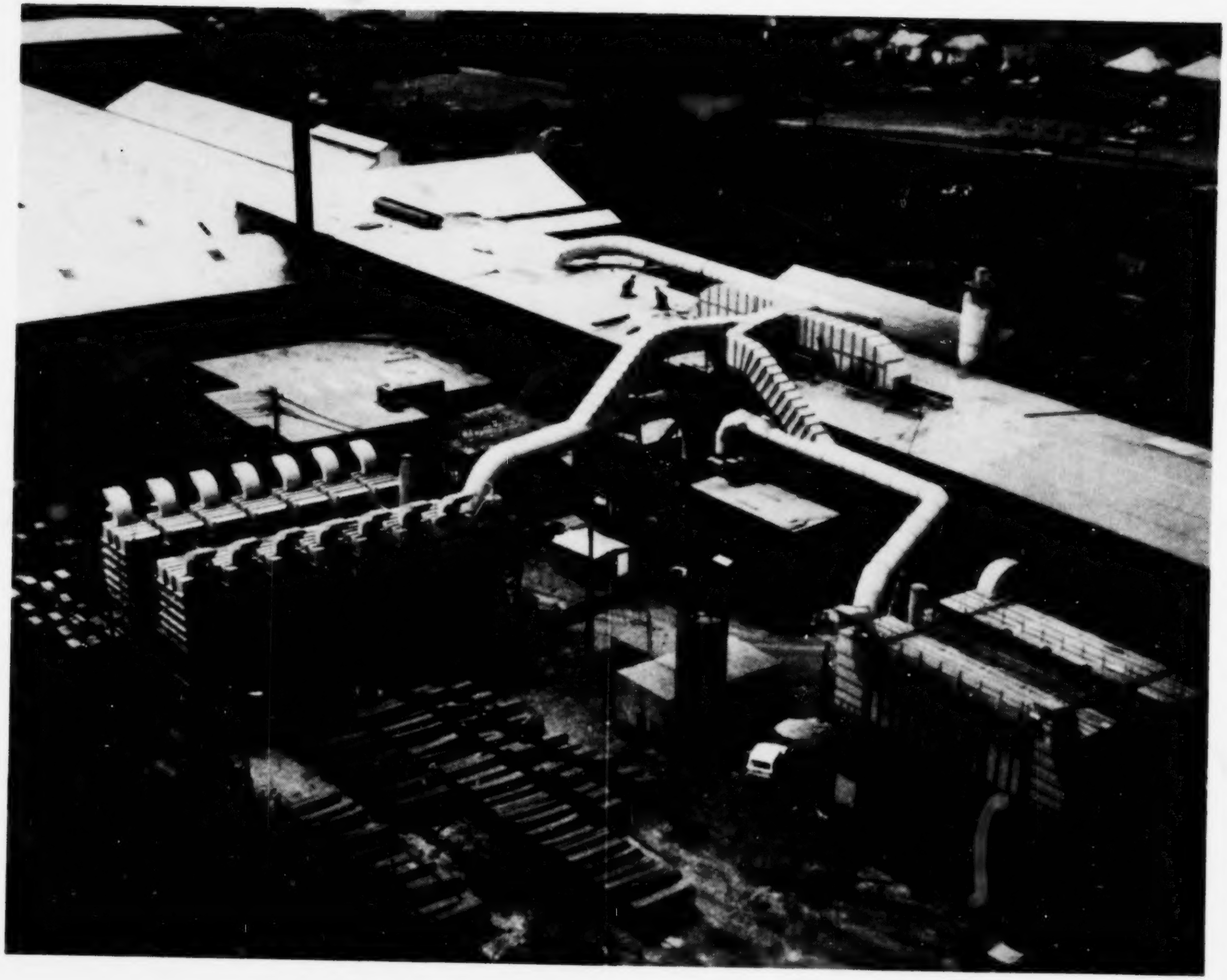

FIGURE 7. AERIAL VIEW OF THE COMPLETED PROJECT.

The absence of limestone in the baghouse dust has helped with dust disposal. The dust is currently being shipped to a recycling operation where zinc is recovered. To aid with dust handling, a centralized pelletizing operation has also been installed. Dust from both baghouses is pelletized.

Current estimates of bag life are 16 months. Bags are currently being replaced on a 16 month cycle even though bag failures are not severe for this duration. Bags are being replaced at this interval to insure good system operation and availability.

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THE PRESENT AND THE FUTURE FOR THE INDUSTRIAL TREATMENT OF FUMES IN THE FRENCH STEEL INDUSTRY

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ABSTRACT

Over the last few years, the French Steel Industry has committed large sums and made an unprecedented technological effort to improve the environment around its plants.

Thus, during the period between 1976-1980, 880 million francs were spent in anti-pollution investments in spite of the unfavorable economic situation.

Two thirds of these investments were devoted to the fight against air pollution and, in several cases, new technologies were used.

This report covers the present situation in seven projects : two coking plants (Sollac and Pont-à-Mousson), three oxygen steel-making shops (Fos, Mondeville and Neuves-Maisons) and two electric steel-making shops (Firminy and Les Dunes).

In each case, the authors analyse the problems to be solved on a technical and regulatory level, the solution applied, especially when technologically unusual, and the results obtained.

From the present situation we can anticipate an evolution of pollution standards and of anti-pollution technology.

THE PRESENT AND THE FUTURE FOR THE INDUSTRIAL TREATMENT OF FUMES IN THE FRENCH STEEL INDUSTRY

INTRODUCTION

In France, the Steel Industry is one of the key industries, employing 120 000 people with an annual turnover of about 50 billion francs for a steel production of 23.4 million tons in 1979.

A considerable effort of modernization is under way. This is illustrated in Table 1 concerning the investments made between 1976 and 1980. This modernization is especially related to the steel-making shops and continuous castings. Many new installations have been started over the last few years.

TABLE 1. INVESTMENTS OF FRENCH STEEL INDUSTRY FOR PRODUCTION OR FOR POLLUTION CONTROL (1976 - 1980)

in 10^6 F	For Production	Pollution Control
Coking plants) Power plants)	890	115
Blast furnaces) Charge preparation)	1 525	102
Steelmaking	2 485	483
Continuous Castings) Rolling mills)	4 670	157
Other	1 130	23
TOTAL :	10 700	880

In spite of the problems encountered in investments because of the present economic situation, the French Steel Industry has not sacrificed environmental protection in and around its plants. Thus, during the 1976-1980 period, the fight against pollution represented 8.2 % of investment spending for the entire profession, although the plan optimistically developed before the energy crisis only allowed for 6.8 %.

Priority is above all given to the control of air pollution (65.5 %), then water pollution (32.8 %) and noise and wastes (1.7 %). The main sectors concerned are the steelshops, the rolling mills and the coking plants.

To illustrate the exceptionnel effort to install air cleaning equipment, a new integrated steelplant of 3 million tons/yr operates 25 dust-separators with a flowrate of 5 million m³/h of fumes which needs an installed power of 10 MV. In this report seven installations for fumes collection and dust removal have been chosen in the three following sectors :

- Coking plants of SOLLAC (Seremange) and of PONT-A-MOUSSON
- Oxygen steelshops of SOLMER (Fos), USINOR (Neuves-Maisons)

and of METALLURGIQUE de NORMANDIE (Mondeville).
- Electric steelshop of CREUSOT LOIRE (Firminy) and CFAS (Dunkerque-Les Dunes).

THE SOLLAC COKING PLANT

SOLLAC started in 1979 at Seremange a battery of 64 coke ovens of the " Compound " type which are capable of producing 600 000 t of coke per year. The ovens are 6.2 m high, 13.7 m long and 0.43 m wide. They are charged by gravity. The coke is unloaded by a mobil coke-car.

The Authorities imposed the following limitations :

- Fumes emitted during charging of the coal and unloading of the coke must be collected and dedusted,

- The dust content in both cases must not exceed 10 mg/m^3N,

- Maintenance and surveillance of the installations must be carefully handled in order to prevent any visible diffused emissions.

In order to respect these conditions, SOLLAC made an agreement of cooperation with the Japanese company NKK and entrusted the study and the construction of dust cleaning equipment to the French company NEU.

During charging, the fumes are collected by two independant circuits : a convention exhaust circuit thanks to ammoniacal water injected under high pressure (42 bar, flowrate 19 m^3/h) and a special exhaust circuit near the charging machine connected to a fixed collector. This one was built all along the battery on the unloading side. When an oven is charged, a telescopic pipe is positionned in front of the oven concerned which has a suction hole in order to collect the fumes created by over pressure and by partial distillation. Fumes are cleaned by a wet ventury-scrubber (Table 2-A).

During unloading, fumes are collected by a mobil hood located at the top of the coke guide. Then they are channelled into a stationary collector and dust is removed in a first separator and in a suction baghouse. The bags are woven with polyester fibers with a small proportion of stainless steel fibers as a precaution against electrostatic charges (Table 2-B)

The Authorities have requested an exhaust as air tight as possible for both cases. This goal has been obtained during charging, where fumes are rarely visible. During unloading, the results are spectacular since nothing escapes from the hood, given its dimensions and its 300 000 m^3/h exhaust rate. As far as dust content is concerned, the standard of 100 mg/m^3 after cleaning is respected with 80 mg/m^3 for charging and 1 to 2 mg/m^3 for unloading.

Over a period of 26 months, the installation was stopped only one day due to an incident on the coke guide. Besides this, none of the bags have been pierced and no condensation have been observed.

Since the results obtained were judged sufficiently successful, the Ministry of Environment discerned its annual prize on the SOLLAC coking plant in 1979 in order to acknowledge their effort made against pollution.

TABLE 2 - FUMES TREATMENT AT THE SOLLAC COKING PLANT

A./CHARGING

Fumes collection	
Charging cycle	7 min 25 s
Fume emission	3 min
Fumes dedusting	
Flowrate	21 000 m^3N/h
Initial dust concentration	5-15 g/m^3
Water flow in the saturator	25 m^3/h
Water flow in the scrubber	36 m^3/h
Pressure drop	1 940 mm of Water
Fumes exhaust	
Centrifugal ventilator	
Nominal flowrate	36 000 m^2/h (530° C)
Motor power	300 kW
Nominal pressure drop	2 480 mm of Water

B./ UNLOADING

Fumes dedusting	
Fumes emission	2 min
Exhausted flowrate	300 000 m^2/h
Initial dust concentration	up to 10 mg/m^2
Pressure drop in the filter	80 mm of Water
Filtering surface	5 150 m
Filter type	polyester 320 g/m^2
Fumes exhaust	
Centrifugal ventilator	300 000 m^2/h (100° C)
Nominal flowrate	300 000 m^2/h (100° C)
Motor power	1 200 kW

THE PONT-A-MOUSSON COKE PLANT

The PONT-A-MOUSSON Company put a battery of 24 " Underjet " coke-ovens into service in 1981. The furnaces are 4.5 m high. The coke is unloaded and quenched by the process developed by the German company ERIN.

This new plant has to respect the following conditions :

- Collection of fumes during charging and unloading,

- Dust content of the fumes rejected to be less than 50 mg/m^3,

- During coke quenching, efficient retention of the particles

(less than 200 g/t of coke),

- Careful maintenance and control of the installations in order to prevent or to eliminate visible emissions.

The hot coke is gathered in a cubic tank which stays in a fixed position during unloading. In order to avoid any notable pollution, the coke guide is hooded and an 8 000 m^3/h ventilator sucks up the fumes.

The dust is removed from the exhaust fumes by a cyclone and a centrifugal scrubber with a water consumption of 150 l/t of coke. These separators are put aboard the coke-car.

After unloading, the ERIN type case, without its lid, is taken to a quenching stand. It is then covered by a second lid equipped with 360 water injection nozzles. Steam and fumes given off are sucked into the bottom of the wagon which has a double bottom (figure 1). Fumes are cleaned then by cyclones.

Later on, when the capacity of the coking plant is doubled, the installation will be equiped for the recovery of energy in the form of steam at 330° C.

This new coke-plant has been operating since the beginning of 1981. Controls have been made on the installation and it is still too soon to tell, especially as certain modifications are being made, but the results obtained at quenching already meet the stipulated limits.

THE SOLMER LD STEEL SHOP. HOT METAL TRANSFER

The SOLMER integrated steel plant has a steel-shop with two LD converters of 280 tons.The supply of hot metal is assured by 450 ton torpedo ladles. The content of these ladles is tapped into 270 ton ladles handled by crane to charge the converters.

During the rapid pouring of the hot metal from one ladle to another, colored fumes are given off. The Authorities have asked that these fumes be collected and the dust removed in order to eliminate their characteristic color. Besides this, the dust content of smoke given off into the air was fixed at 120 mg/m^3N.

The SOLMER company has conceived of and realized a removable hood which closes off the area of smoke emission as tightly as possible at the impact of the hot metal in the ladle. This hood overhangs the pit where the ladle to be filled is located. It is made up of four removable parts : two parts, on each side of the rails, which swing up to form the top of the hood and two side-panels which are let down to close the hood. Fumes collected during the transfer at the rate of 200 000 m^3N/h are cleaned first by cyclone to eliminate the large incandescent particles, and then by filter bags, furnished by the french company AIR INDUSTRIE.

The depression in the hood is such that no smoke can escape

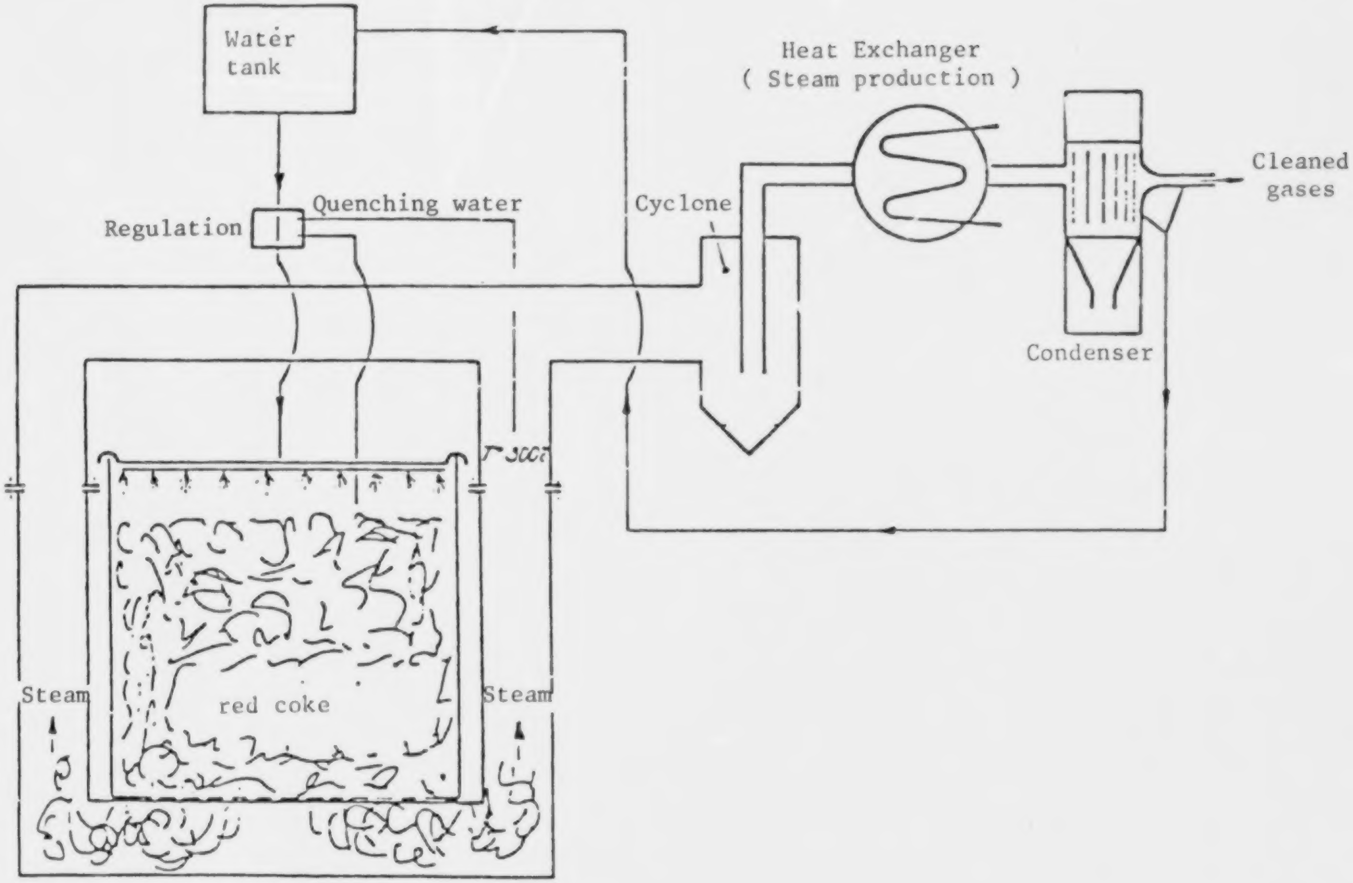
Water tank
Regulation
Quenching water
T 300°C
Cyclone
Heat Exchanger
(Steam production)
Condenser
Cleaned gases
Steam
red coke
Steam

FIGURE 1. THE " ERIN " COKE QUENCHING PROCESS AT PONT-A-MOUSSON

during pouring of the hot metal. This is also true even when a side panel is accidentally not in place. Since Fumes are cleaned by filtering, the dust content limit of 120 mg/m³ is respected with no problem. Adjustments had to be made on the opening system for the largest piece of the hood, but now the installation is quite satisfactory.

THE USINOR Q-BOP STEELSHOP AT NEUVES MAISONS

The USINOR company started a new steel plant with two 125 ton converters in July 1979 at Neuves-Maisons. These converters use the Q-BOP process and refine phosphorous hot metal. The Authorities enforced application of the French regulations concerning red fumes in order to obtain colorless fumes at all times and to respect the dust content limitation of 120 mg/m³N on the average during the blow.

All of the installation was built by LURGI.

Collecting converter gases during blowing is now a classic operation. But it was done at Neuves-Maisons with partial combustion of the gases ($\lambda = 0.3$), an operation with suppressed combustion is foreseen in order to recover and valorize these converter gases in the plant.

Neuves-Maisons is the first steel shop in the world to operate dry electrostatic precipitators with fumes from bottom-blown converters. The three-field precipitators are installed on a platform outside. Each one is a 16 m long cylinder having an inside diameter of 10.8 m (figure 2). The gas flow was studied to avoid turbulence and thus a mixing of the different flows alternately rich in air or in CO and H_2 especially at the beginning and at the end of each blowing cycle.

TABLE 3- CONTROL OF CONVERTER FUMES AT NEUVES MAISONS

Electrostatic precipitators	
Number of fields	3
Secondary voltage	60 kV for field Nr. 1 35 kV for fields Nr.2 and 3
Secondary intensity	400mA
Fumes extraction	
Nominal flow	340 000 m³/h
Nominal temperature	150° C
Motor power	250 kW

Since no installations can be totally protected from an accidental explosion, the electrofilters are designed to resist an over pressure of 2 bars and they are supplied with safety valves on the entry and exit cones. However, the gases are continuously analysed and the safety systems are set off when there is

$CO > 6\,\%$ $O_2 > 4\,\%$ $H_2/CO > 0.14$

or when $CO > 9\,\%$ $O_2 > 4\,\%$

The extraction ventilator is axial in order to avoid any risk

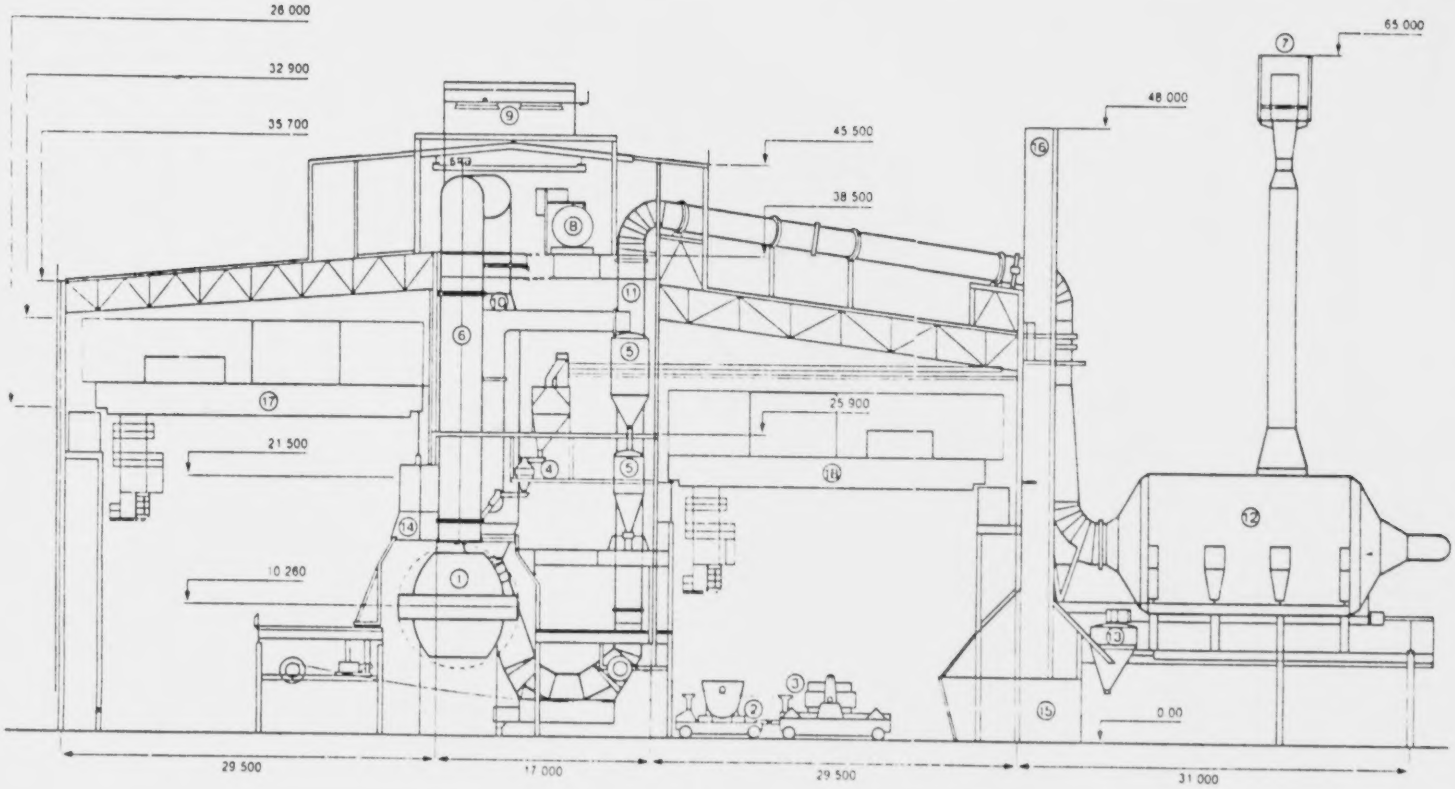
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FIGURE 2. THE NEW USINOR Q-BOP STEELSHOP AT NEUVES-MAISONS

1. Q-BOP converters of 125t
12. Electrostatic precipitators

of destruction by allowing an easy displacement of a possible shock wave coming from an explosion in the precipitators.

Till now, the results obtained for both collection and dust control satisfy the standards set by Administration.

THE LD-AC STEELSHOP OF SMN-HOT METAL CHARGING EMISSION CONTROL

The new steelshop of the METALLURGIQUE de NORMANDIE (SMN) at Mondeville has two 100 ton converters which were started in 1977. They are top blown converters and treat high phosphorous hot metal. They are equipped for primary fumes with a full combustion exhaust and a wet dedusting system.

The Authorities have imposed collection and cleaning of fumes emitted during the charging of the converters with the following double goal : residual dust content less than 120 mg/m^3N and permanent absence of colored fumes released into the atmosphere. This last constraint has imposed, in fact, to respect a maximum dust content of 50 mg/m^3.

When liquid hot metal is poured into a hot converter charged with scrap, impressive red fumes come out of its mouth. Two reactions generally come into play : on one hand, oxidation of the metal and emission of graphite, as during the transfer of hot metal from one ladle to another; on the other hand, the quasi-explosive combustion of part of the oils and greases contained in the scrap already charged. At Mondeville, refining of high phosphorous hot metal is made in two phases and the end slag is recycled. It stays in the converter between two cycles and, as it is highly oxidized, it reacts with the carbon of the hot metal with increased fumes emission during charging. These local conditions explain why it is particularly necessary in this shop to collect and dedust these fumes.

To this end, the converter hood is doubled with a secondary suction circuit which is used during charging. Flames and fumes are collected by a frontal hood extended by chains. The actual exhaust rate of this hood is about 25 m/s with a dynamic depression of 30 milimeters of water. The frontal hood and the secondary duct are connected to the primary fumes circuit of each converter which is highly favorable since collection during blowing is made with full combustion (figure 3).

All of the observations made show that the fumes are almost completely collected. The intake of the frontal hood is such that any small emission rising in front of the chain curtain is drawn through it. When the reaction in the converter becomes too violent, the crane operators can reduce the hot metal flow, which is normally 35 t/min in this shop.

Then, these fumes are dedusted with the " Kinpactor " venturi-scrubber, which is also used for the primary fumes. This equipment was made by AMERICAN AIR FILTER.

After adjustement of the ventilator and the scrubber, especially by reduction of the flow of water injected, the performances demanded by the Authorities have been respected with a good reliability since four years.

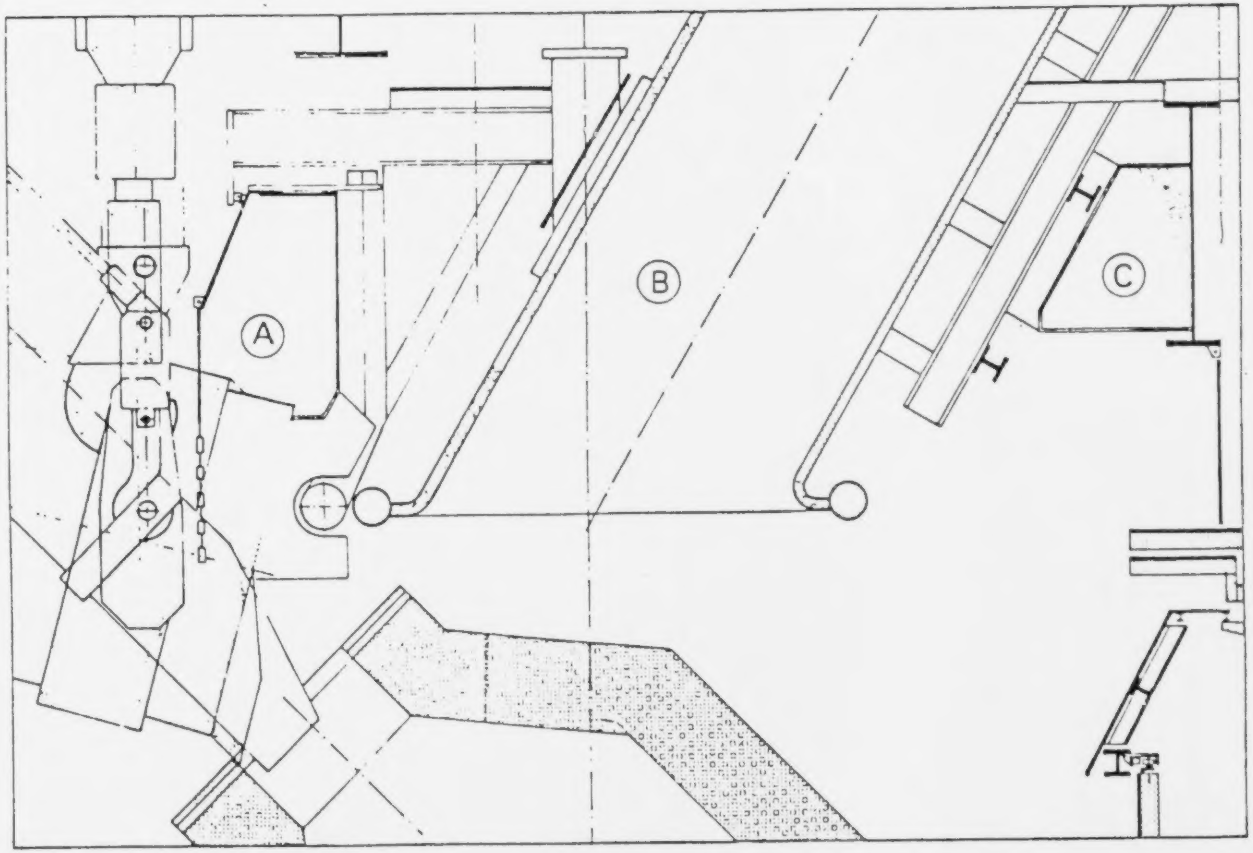

FIGURE 3. SECONDARY FUMES COLLECTION SYSTEM AT MONDEVILLE STEELSHOP

A. Charging hood
B. Primary fumes hood
C. Tapping hood

With a pressure drop of 1700-1800 mm of water in the scrubber, the measured dust contents are now in the range of 20-40 mg/m^3.

THE CREUSOT LOIRE ELECTRIC STEELSHOP AT FIRMINY

The Firminy steelshop operates 3 arc furnaces. The 35t furnace which specialized in stainless steelmaking, was equipped with a dust control system in 1978. This furnace has the following characteristics :

- inner vesser diameter = 4.2 m
- transformer power = 17 MW
- 5 heats per day.

The following standards have been set by local Administration :

- efficiency of fumes collected so that, except on rare occasions, no fumes are visible and a 90% minimal efficiency is required for fumes collected in the hood;

- residual dust content of less than 10 mg/m^3N on the average for a cycle, not taking into account the possible dilution in the cleaning system for the whole steelshop. The dust content between 10 and 20 mg/m^3N is tolerated for only 28 days per year.

In any furnace producing special steels, it is necessary to reduce the risks of oxidation of the charge by air intake. Because of this, the operators gave up the idea of a fourth hole and chose instead a collection by a canopy hood divided into three parts : charging, melting-refining and tapping hoods are separate since, in contrast with the usual practice, the vessel moves along the floor for charging (figure 4).

Several measurements have been made by LECES, the French organization specializing in pollution studies in the Steel Industry. It has been shown that the 90% collection efficiency in the hood demanded by the Administration has been respected and that it is even possible to save energy by modulating the exhaust rate depending on the fumes output (200,000 to 400,000 m^3/h). Table 4 shows, as an example, the results obtained on a heat by controlling the dust balance.

TABLE 4. DUST BALANCE OF THE 35 TON ARC FURNACE AT FIRMINY

Phase	Collected in baghouse	Settling in bay	Released outside	Collection yield
Melting	108 kg	2.5 kg	10.2 kg	90 %
Refining	300 kg	0.2 kg	18.5 kg	94 %
Tapping	20 kg	1.0 kg	0.6 kg	93 %
TOTAL :	428 kg	3.7 kg	29.3 kg	93 %

Dust separator is a baghouse using the FLAKT technique of " superpulse " (felt filters and pressure jet cleaning system). The operators

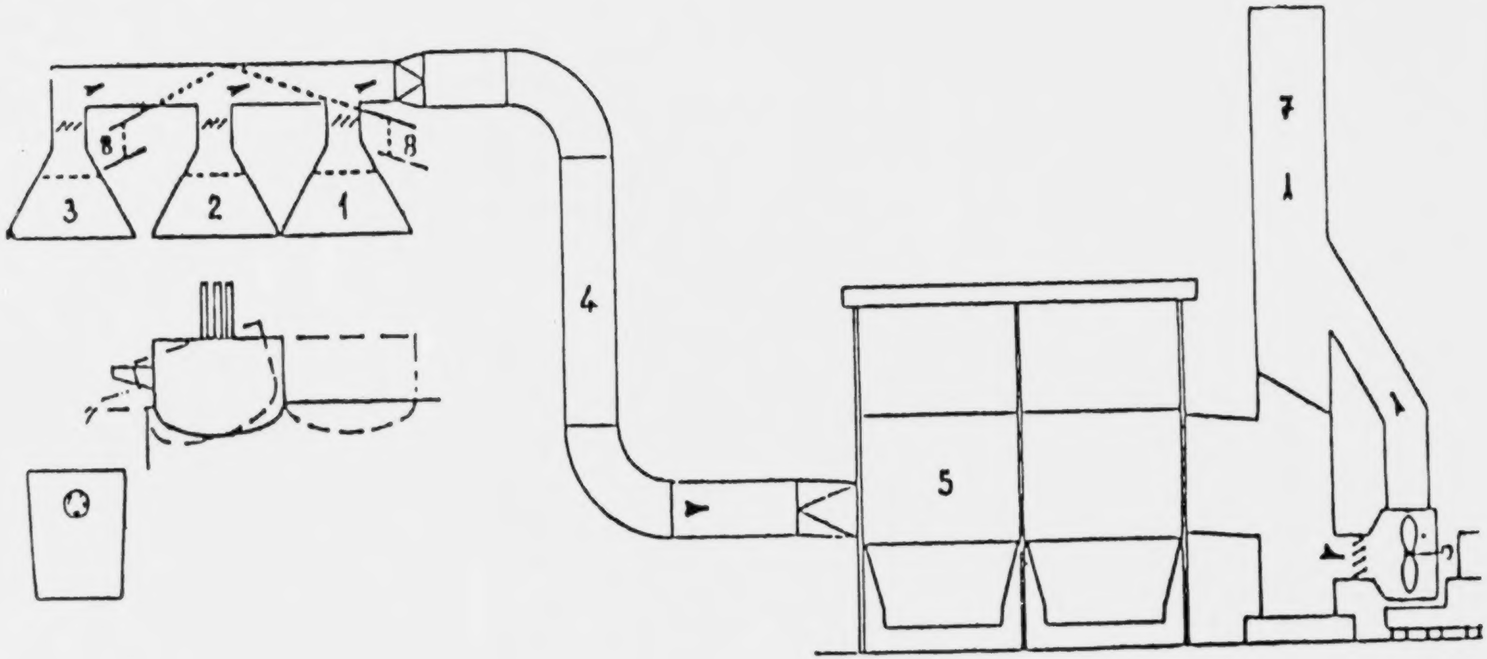

FIGURE 4. FUMES CLEANING INSTALLATION IN THE 35t EAF AT FIRMINY

1. Charging hood
2. Melting hood
3. Tapping hood
4. Fumes duct
5. Bag filter plant
6. Exhaust fan
7. Stack
8. Dampers

had no trouble respecting the limit of 20 mg/m³N. Simulated accidents have shown that with two bags taken off, the dust content varies between 2 and 15 mg/m³. The installation is very satisfactory and the only adjustment concerned the reduction of electrical consumption and noise insulation of the fume stack.

THE ELECTRIC STEELSHOP OF CFAS - LES DUNES

The works in Les Dunes near Dunkirk has installed a 80 ton UHP arc furnace in 1978. It is located in an individual bay which is completely closed. This furnace has the following characteristics :

- vessel diameter	5.8 m
- power	48 MVA
- nominal capacity	80 t
- 12 heats per day.	

The local standards are the same as in Firminy (no visible emission, dust content of rejected fumes less than 20 mg/m³N.

The furnace is equipped with a classical fourth hole and with canopy hoods. The roof being completely closed above the furnace, no fumes can escape in the atmosphere. The results are thus excellent as far as the environment is concerned, but under certain unfavorable conditions fumes stagnate in the bay (difficulty of exploitation of the regulation of the installation).

Primary and secondary fumes are mixed before cleaning. Dust control is done by filtering on felt-bags using the FLAKT technique of " superpulse " already presented for the Firminy baghouse (Table 5). The fumes are extracted by a 400,000 m³/h ventilator placed downhill from the baghouse and they are released into the atmosphere through a stack which has an opacimeter installed on it for continuous control.

TABLE 5 - FUMES CLEANING INSTALLATION IN THE ELECTRIC SHOPS AT FIRMINY OR LES DUNES

Exhaust	
Nominal output	400,000 / 480,000 m³/h (135° C)
Power of motors	2 x 400 kW (Firminy) 4 x 250 kW (Les dunes)
Cleaning equipment	
Bag type	polyester-felt bags (0.5 kg/m²)
Bag dimensions	Ø 0.3 m h = 5 m
Filtering surface	2 690 m²
Pressure drop in filter	130 - 240 mm of water
Bag cleaning system	sonic cleaning at low pressure (1.7 bar)

Periodicaly dust contents measurements and opacimetric controls are made and they show that the standard of 20 mg/m³N has been strictly respected except for incidents in the baghouse.

The installation for the treatment and cleaning of fumes works under harsh conditions since the UHP furnace has a high productivity. Twice, violent reactions in the charge have caused the destruction of many of the bags.

CONCLUSIONS AND PROSPECTS

We have just presented seven installations for air pollution control now in operation in the French Steel Industry. After the necessary operating adjustments are made, their results meet the standards set by the Administration.

A considerable effort has been made in the last few years. However as far as environmental protection is concerned, the seven examples given are not truly representative of the entire French Steel Industry, as the list presented is not exhaustive. There also remain plants with much less satisfactory pollution control equipment.

It must also be noted that we have focussed our attention on the difficult problems linked to the collection and cleaning of fumes.

Generally, the governments will be more and more demanding in the future and will impose strict controls of emissions into the atmosphere, not only for dust but also for certain pollutants such as heavy metals, hydrocarbons, gases and so on.

Other constraints than those imposed by the environment will be more and more often imposed, for better health and working conditions or for saving of raw materials and energy.

In expanding industries, it will be to the interest of the managers to change their methods of production and to adopt what has been called " clean technologies ", while associating automation with it. Such an evolution will probably be slower in the Steel Industry, given the present economic situation and the large investments needed for construction of production units.

For many years yet, a large part of production will thus be assured by plants of the type which presently exist and the French examples, which we have given, show that it is possible to successfully protect the environment.

MODELING OF HOOD CONTROL OF BLAST FURNACE CASTING EMISSIONS

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ABSTRACT

A laboratory scale model test technique has been developed to simulate the thermal and flow characteristics of blast furnace casting emissions and to evaluate the performance of potential hood collection devices. The test system utilizes fresh water as the source fluid to model casting emissions and concentrated sodium chloride solution to model the denser surrounding environment. Excellent flow visualization is obtained through the generation of light reflecting hydrogen bubbles in the source fluid stream by electrolysis. Application of the technique to qualitative evaluation of hood performance is illustrated by an example. In addition, use of the technique to generate numerical values of hood collection efficiencies is described.

INTRODUCTION

During tapping of molten iron from blast furnaces, emissions are released due to exposure to the atmosphere. The magnitude of these emissions, which are primarily fugitive in nature, can vary considerably from blast furnace to blast furnace or between casts from the same furnace. Significant efforts to curtail these emissions were initiated in the U.S. during the last 3-4 years. (For a review of the status of cast house control technology in the U.S., Japan and Western Europe, see References 1, 2, 3).

Techniques that have been developed to control blast furnace casting emissions include total evacuation systems, non-capture shrouding systems and local hood systems. Total evacuation systems effecting 60 or more cast house volume air changes per hour are expected to be effective. Due to the large gas volumes handled, these systems are highly energy intensive. The non-capture shrouding method is a proprietary technology developed by the Jones and Laughlin Steel Corporation in the fall of 1980. A system that has been successfully used by the Japanese over the years consists of local hoods over the primary emission sources (such as tap holes, troughs and spouts) and dome shaped covers over runners. This primary capture system might be supplemented by a secondary capture system that controls emissions from the tap hole operations. The refractory-lined hoods and covers are designed so as to permit easy removal by overhead cranes for maintenance and repairs. These systems require large areas for the storage of spare parts and maintenance equipment, laying of take-off ducts and the movement of cranes. The frequency and the extent of maintenance required on the close fitting hoods and runner covers will have to be established under U.S. furnace operating conditions before implementing this technology in this country. Further, more than 90% of the existing blast furnaces in the U.S. are single tap hole furnaces as opposed to the multiple tap hole furnaces in Japan. This reduces the time available for removal or repositioning of close fitting covers and hoods in the area of the trough and tap hole between casts. The solution to this may be the application of hoods with retractable curtains for capture of emissions from this area. However, the effectiveness of such a system must be established by tests before final design.

Hoods at or near the truss level have been attempted in a few North American blast furnaces (References 1, 3). Performance of these hoods in general have been unsatisfactory. If, with proper design and location of these hoods and the use of deflectors or guide plates, satisfactory capture of emissions from the major sources (tap hole, trough, skimmer and spouts) can be achieved, then this system could prove to be the optimal choice for retrofitting to many of the existing cast houses in the U.S. and possibly for installation in some of the new cast houses. However, it should be noted that the capture efficiency of hoods positioned several feet above the surface of the molten metal could be very sensitive to their location and design features such as hood skirting. Scale model tests that predict hood performance and optimize hood design can provide valuable information required to make decisions in cases of this sort.

The present paper describes a scale model test system based on the principles of dimensional analysis to characterize casting emissions and to evaluate the effectiveness of different hood capture systems.

THE MODEL TEST SYSTEM AND TEST PROCEDURE

Model development was based on the primary scaling parameters applicable to buoyant turbulent plumes. These are discussed in the following section. Scaling considerations mandated the use of a liquid model as opposed to gas models. Tap water with a trace of anhydrous sodium sulphate was selected as the source fluid to model the casting emissions and concentrated brine solution was chosen to model the denser surrounding medium. Excellent flow visualization is obtained by the generation of tiny hydrogen bubbles (less than one hundredth of an inch in diameter) in the source stream by electrolysis. The hydrogen bubbles reflect light beams from high intensity lamps so that the plume flow can be observed and photographed.

Figure 1 shows a schematic of the laboratory test system. Source fluid is pumped through the air eliminator and the hydrogen bubble generator into the lower chamber of the blast furnace model. As the fluid flows through the bubble generator, hydrogen bubbles are generated by electrolysis. The bubble-water mixture rises through controlled openings in the trough and runner generating the model plumes. By properly scaling the source emission flow rates and the densities of the source and surrounding fluids, and by

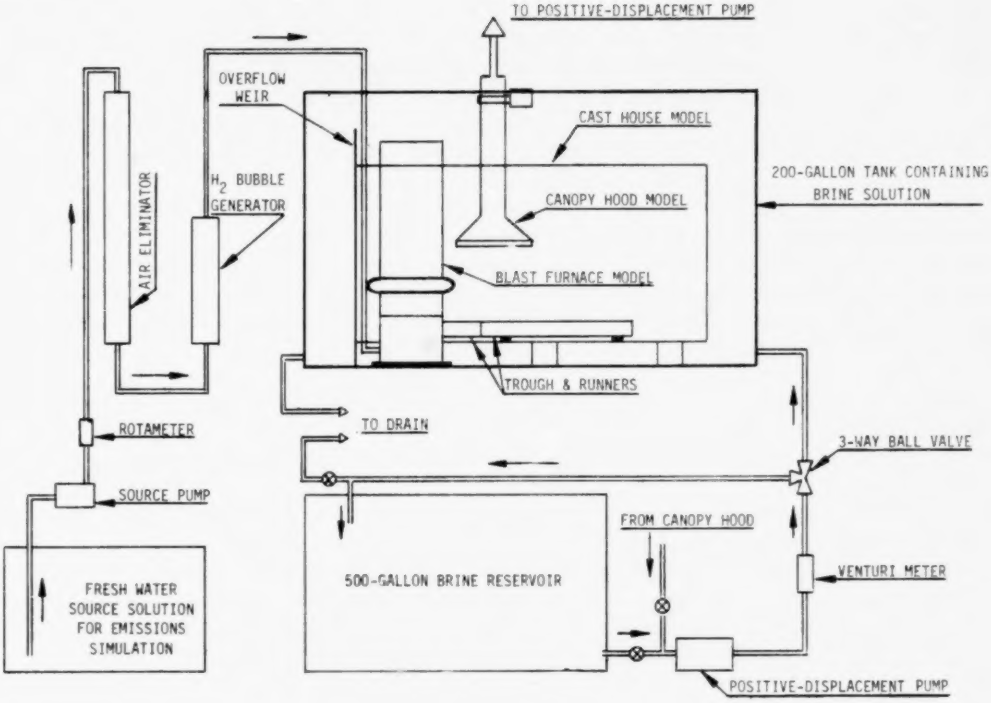
TO POSITIVE-DISPLACEMENT PUMP
OVERFLOW WEIR
CAST HOUSE MODEL
200-GALLON TANK CONTAINING BRINE SOLUTION
H_2 BUBBLE GENERATOR
AIR ELIMINATOR
CANOPY HOOD MODEL
BLAST FURNACE MODEL
TROUGH & RUNNERS
TO DRAIN
ROTAMETER
3-WAY BALL VALVE
SOURCE PUMP
FROM CANOPY HOOD
500-GALLON BRINE RESERVOIR
VENTURI METER
FRESH WATER SOURCE SOLUTION FOR EMISSIONS SIMULATION
POSITIVE-DISPLACEMENT PUMP

Figure 1. Schematic of Laboratory Test System

adjusting the opening areas of the runners and the trough, the model plumes were tuned to simulate the important characteristics of the full-scale emissions. (During the course of the experiments, the specific gravity of the surrounding fluid was constantly checked and corrected when necessary.) To evaluate the performance of a hood, the variable speed P.D. pump was set at the scaled volume flow rate evacuating fluid through the hood and discharging to the brine reservoir or to drain. For each case, a qualitative evaluation of the collection efficiency of a hood could be made by observing and comparing the plume rise/spread phenomena with no hood and then with the hood in position and the evacuation pump on and then off.

SCALING CONSIDERATIONS

The relevant parameters for modeling buoyant plumes are Grashof number (Gr), Reynolds number (Re) and Froude number (Fr). These are defined as

$$Gr = \frac{g \times \beta \times (T_s - T_\infty) \times D_s^3}{\nu_s^2} = \frac{g \times (\rho_\infty - \rho_s) \times D_s^3}{\rho_\infty \times \nu_s^2}, \text{ for ideal gases}$$

$$Re = \frac{U_s \times D_s}{\nu_s}$$

$$Fr = \frac{U_s}{\sqrt{g \times D_s}} = \frac{Re}{\sqrt{Gr \times \frac{\rho_\infty}{\rho_\infty - \rho_s}}}$$

Most plume problems are treated in terms of the densimetric Froude number,

$$Fr = \frac{U_s}{\sqrt{g \times D_s \times \frac{\rho_\infty - \rho_s}{\rho_\infty}}} = \frac{Re}{\sqrt{Gr}}$$

For values of ρ_s significantly different from ρ_∞, a more accurate expression for Froude number is

$$Fr = \frac{U_s}{\sqrt{g \times D_s \times \frac{\rho_\infty - \rho_s}{\frac{\rho_\infty}{2} + \rho_s}}}, \text{ Reference 4}$$

Scaling in terms of the densimetric Froude number will insure basic similarity between plumes. In addition, it is necessary to ensure that model plume Reynolds numbers are large enough to be in the turbulent regime since the full-scale plumes are always turbulent.

FIELD OBSERVATIONS AND DERIVATION OF FULL-SCALE DATA

Full-scale data for this study was obtained by making field observations of actual emissions from a local cast house (the No. 3 cast house at the East Chicago plant of J & L Steel Corporation). Emissions from 4 casts were observed over a 3-day period. The casts differed significantly in duration and were performed under significantly different ambient conditions, so that the observations covered a large range of possible emission characteristics. The tasks involved in obtaining field data included motion photography of the dust plume generated at the notch and along the runners, visual observations

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Symbols.

D = Diameter or characteristic length; g = Acceleration due to gravity;
Q = Source emission rate or hood evacuation rate;
T = Absolute temperature; U = Flow velocity;
ρ = Specific gravity of fluid; ν = Kinematic viscosity;
β = Coefficient of volume expansion

Subscripts.

f → full-scale; m → model; s → source fluid;
∞ → undisturbed surrounding fluid; s,f → source, full-scale;
s,m → source, model; ∞,m → surrounding fluid, model

of typical operating practice, and documentation of tons poured, start and finish times, atmospheric conditions, existing cross-drafts during casting, and other pertinent observations. The most significant task was motion photography of the generated plume. The intent of this photography was to document the expansion of the plume as it rises and the rate of rise and bouyancy of the plume.

The motion photography was also supplemented by some still photography which among other things, was used to document the nature and location of building openings permitting air infiltration into the cast house. These openings along with the other important geometric details of the cast house were later incorporated in an approximate sense into the laboratory model which was fabricated to a length scale of 1:45 (model: full-scale) using clear Plexiglas sheets.

Emissions modeled in the present study included those during initiation of iron flow to No. 1 ladle, dumping (draining) of the trough to No. 1 ladle and the lancing operation. Average values of fume rise velocities during initiation of iron flow to ladle No. 1 and trough dumping were estimated to be between 600 and 700 fpm from the analysis of the movie films and the field observations. Rise velocities of lancing fumes were approximately half of these values. Mean values of the effective source areas for emissions of the former two events were also determined by analysis of the movie films and the dimensions of the trough and runners obtained from shop drawings. Using these data, the mean values of source emission rates for these two events were calculated as 9000 acfm and 18,000 acfm respectively. Determination of the effective source area for the emissions during lancing was more difficult. However, this was also roughly estimated by analyzing the movie films, from which the emission rate for lancing was calculated as 4000 acfm. To ensure that this value was conservative, a lower bound for the emissions was also determined by an indirect calculation based on the oxygen consumption during the lancing operation. This was obtained as ~ 2250 acfm. The value of 4000 acfm calculated as explained above was therefore considered conservative and accurate enough for modeling purposes.

SELECTION AND DESIGN OF MODEL HOODS

From drawings of the full-scale cast house, full-scale hood dimensions were determined such that the hoods appeared to be compatible with the existing structure while providing (potentially) reasonable capture of the emissions being considered. Locations of the three hoods inside the full-scale cast house, for which model testing was performed, are illustrated in Figures 2 through 5.

The large hood at truss level spans, longitudinally, two bays between the steel trusses. It covers the major source emission areas associated with trough dumping and iron flow to the No. 1 ladle. This hood was expected to be efficient in capturing fumes from the main trough, the No. 1 ladle runner, the runner used for trough dumping to the No. 1 ladle, and possibly the iron notch. Since the emissions during trough dumping and iron flow to the ladles peak only for very short durations, it was envisioned that this hood, with its large plenum, would contain the fumes and provide satisfactory performance

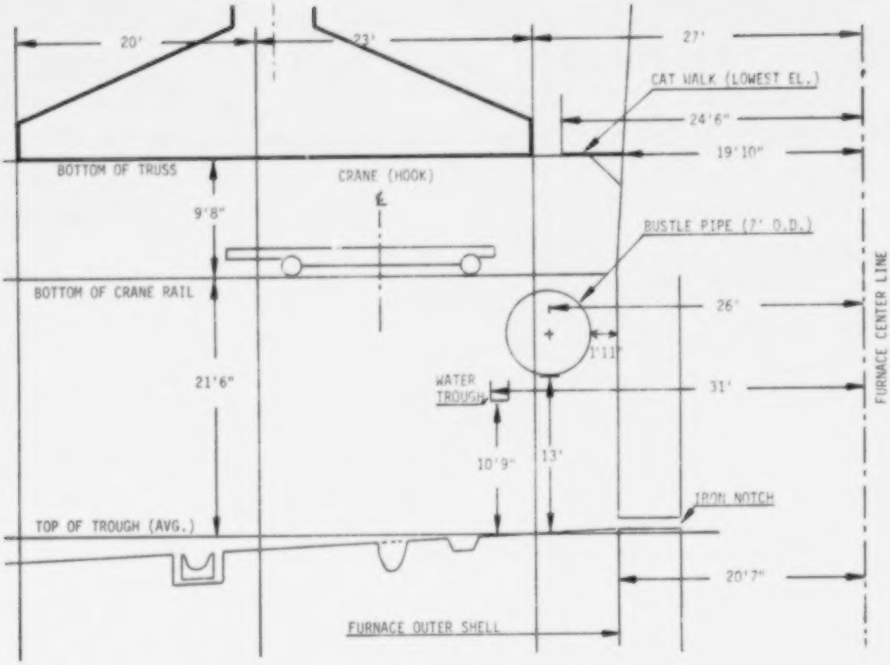
20'
23'
27'
CAT WALK (LOWEST EL.)
24'6"
19'10"
BOTTOM OF TRUSS
CRANE (HOOK)
℄
9'8"
BUSTLE PIPE (7' O.D.)
BOTTOM OF CRANE RAIL
26'
1'11"
21'6"
WATER TROUGH
31'
FURNACE CENTER LINE
10'9"
13'
IRON NOTCH
TOP OF TROUGH (AVG.)
20'7"
FURNACE OUTER SHELL

Figure 2. Position of Large Hood at Truss Level - Elevation View

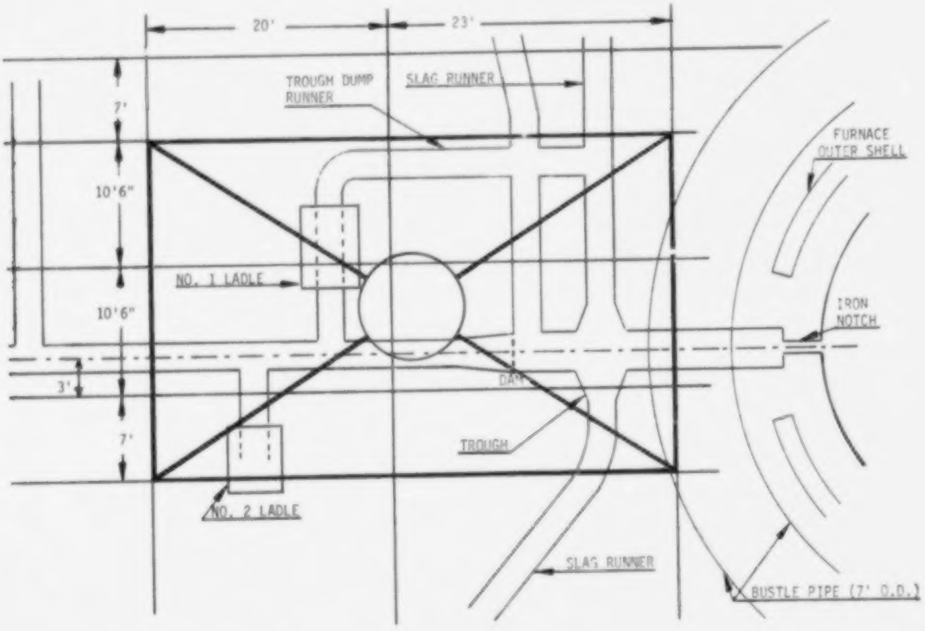
20'
23'
7'
TROUGH DUMP RUNNER
SLAG RUNNER
10'6"
FURNACE OUTER SHELL
NO. 1 LADLE
10'6"
IRON NOTCH
3'
DA
7'
TROUGH
NO. 2 LADLE
SLAG RUNNER
BUSTLE PIPE (7' O.D.)

Figure 3. Position of Large Hood at Truss Level - Plan View

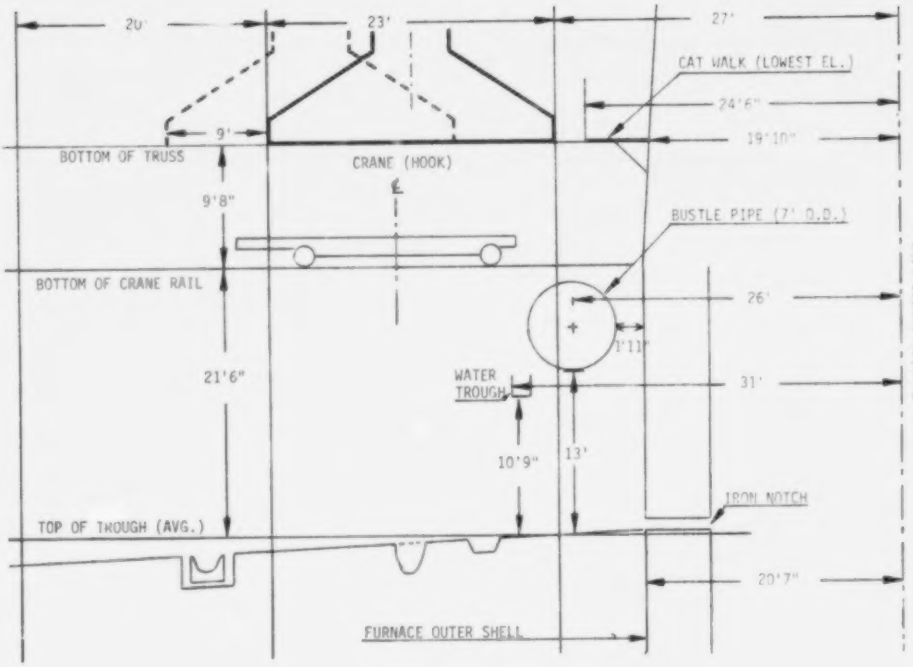
20'
23'
27'
CAT WALK (LOWEST EL.)
24'6"
9'
19'10"
BOTTOM OF TRUSS
CRANE (HOOK)
℄
9'8"
BUSTLE PIPE (7' O.D.)
BOTTOM OF CRANE RAIL
26'
1'11"
FURNACE CENTER LINE
WATER TROUGH
31'
21'6"
10'9"
13'
IRON NOTCH
TOP OF TROUGH (AVG.)
20'7"
FURNACE OUTER SHELL

Figure 4. Positions of Small Hood at Truss Level - Elevation View

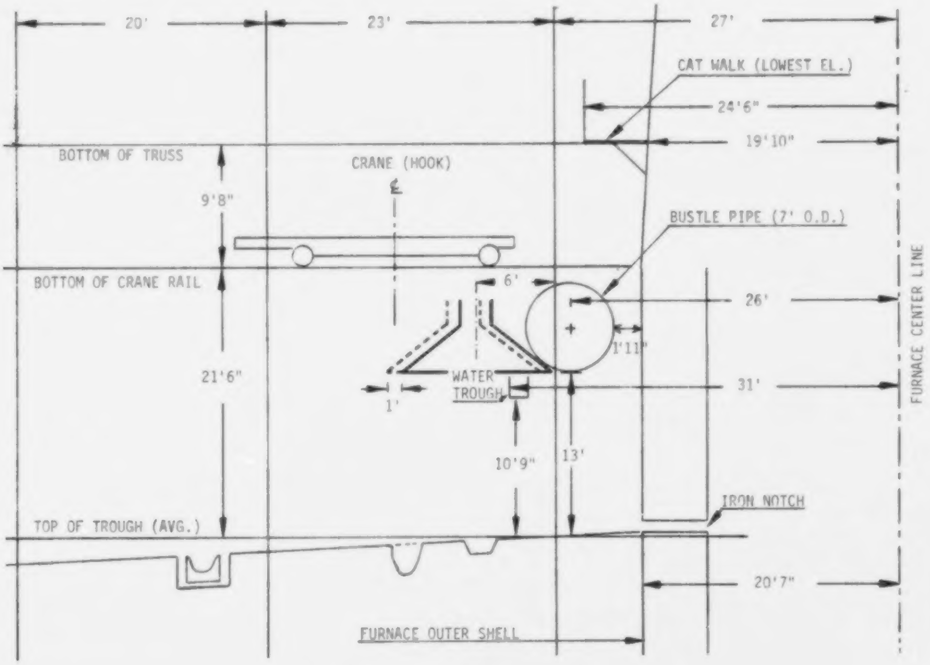
20'
23'
27'
CAT WALK (LOWEST EL.)
24'6"
19'10"
BOTTOM OF TRUSS
CRANE (HOOK)
℄
9'8"
BUSTLE PIPE (7' O.D.)
BOTTOM OF CRANE RAIL
6'
26'
1'11"
FURNACE CENTER LINE
21'6"
WATER TROUGH
1'
31'
10'9"
13'
IRON NOTCH
TOP OF TROUGH (AVG.)
20'7"
FURNACE OUTER SHELL

Figure 5. Positions of Low-Level Hood - Elevation View

even at face velocities somewhat lower than conventional values.

The small hood at truss level has the same lateral dimension as the large hood, but its length is equivalent to only one bay between adjacent steel trusses. This hood was of interest because, with proper positioning over the various emission sources and somewhat high face velocities, it was expected to perform satisfactorily. This hood has a face area approximately half that of the larger hood. It was tested in two locations, as shown in Figure 4.

Dimensions of the low-level hood (at the level of the bustle pipe) are severely constrained by the area available at this level near the furnace. Without compromising too much on its location (which was considered critical), the proper design appeared to be one with a face area of 13 feet x 13 feet. This hood was tested in two positions, one right against the bustle pipe and the other slightly offset from the bustle pipe (see Figure 5).

Take-off ducts for the model hoods were sized such that the scaled flow velocities in the full-scale ducts fall within the conventional range, 3500 to 7000 fpm. The geometric configurations for the hood take-offs were not otherwise modeled.

MODEL SYSTEM PARAMETERS

First, the maximum value of full-scale hood flow rate to be modeled was determined by taking the product of the plenum area of the largest hood and a reasonable value of face velocity (125 fpm) at the plenum. This was calculated as ~ 150,000 acfm. The corresponding value of model hood flow rate was calculated as 18.8 gpm using a volume flow rate scale of 1:60,000 (model: full-scale). The length scale of the model having been selected as 1:45 (as cited earlier), the remaining model parameters were calculated as illustrated in the following.

$$\text{Velocity scale} \equiv \frac{U_{s,m}}{U_{s,f}} = \frac{Q_{s,m}}{Q_{s,f}} \times \frac{D^2_{s,f}}{D^2_{s,m}} = \frac{1}{30} \qquad \text{(a)}$$

For equality of densimetric Froude numbers,

$$\frac{D_{s,m} \times \left[\dfrac{\rho_\infty - \rho_s}{\dfrac{\rho_\infty}{2} + \rho_s}\right]_m}{D_{s,f} \times \left[\dfrac{\rho_\infty - \rho_s}{\dfrac{\rho_\infty}{2} + \rho_s}\right]_f} = \left(\frac{U_{s,m}}{U_{s,f}}\right)^2 = \frac{1}{900} \qquad \text{(b)}$$

Assuming ideal gas behavior,

$$\left[\frac{\rho_\infty - \rho_s}{\dfrac{\rho_\infty}{2} + \rho_s}\right]_f = \frac{2(T_s - T_\infty)}{2\,T_\infty + T_s} \qquad \text{(c)}$$

Calculation of Liquid Densities for Modeling Initiation of Iron Flow to No. 1 Ladle and Dumping of the Trough

Substituting reasonable values for T_s and T_∞ (1460°R and 560°R respectively) into equation (c),

$$\left[\frac{\rho_\infty - \rho_s}{\frac{\rho_\infty}{2} + \rho_s}\right]_f = 0.698$$

From equation (b),

$$\left[\frac{\rho_\infty - \rho_s}{\frac{\rho_\infty}{2} + \rho_s}\right]_m = \frac{1}{900} \times \frac{45}{1} \times .698 = 0.035$$

Specific gravity of the model source fluid was determined as 1.005 for proper concentration of sodium sulphate to give trouble free generation of hydrogen bubbles. With this value of $\rho_{s,m}$ the specific gravity of the brine solution in the tank $\rho_{\infty,m}$ was calculated as 1.059.

Calculation of Liquid Densities for Modeling Lancing

Values of volume rate scale and length scale for lancing were kept the same as for the other events. Therefore the velocity scale also remained unchanged.

$$\frac{\left[U_{s,m}\right]_{\text{lancing}}}{\left[U_{s,m}\right]_{\text{trough dumping}}} = \frac{\left[U_{s,f}\right]_{\text{lancing}}}{\left[U_{s,f}\right]_{\text{trough dumping}}} = \frac{1}{2}\text{, from field data}$$

and

$$\frac{\left[\frac{\rho_\infty - \rho_s}{\frac{\rho_\infty}{2} + \rho_s}\right]_{m,\text{ lancing}}}{\left[\frac{\rho_\infty - \rho_s}{\frac{\rho_\infty}{2} + \rho_s}\right]_{m,\text{ trough dumping}}} = \frac{\left[U_{s,m}\right]^2_{\text{lancing}}}{\left[U_{s,m}\right]^2_{\text{trough dumping}}} = \frac{1}{4}$$

With $\rho_{s,m} = 1.005$ and $(\rho_{\infty,m})_{\text{trough dumping}} = 1.059$

one obtains $(\rho_{\infty,m})_{\text{lancing}} = 1.018$

Calculation of Source Emission Rates

Table 1 gives values of full-scale source emission rates (as cited earlier) and the corresponding values of model source flow rates based upon the volume rate scale of 1:60,000.

TABLE 1. SOURCE EMISSION FLOW RATES

Event	Estimated Full-Scale Source Emission Rate acfm	Calculated Model Source Flow Rate gpm
Lancing to open notch	4,000	0.5
Initiation of iron flow to ladle No. 1	9,000	1.2
Dumping of trough to ladle No. 1	18,000	2.2

Check for Similarity of Flow Regimes

For similarity of flow regimes, it is important to ensure that the model plume Reynolds numbers close to the source are well above the critical value of 300-600 (Reference 5). Approximate values of model plume Reynolds numbers can be obtained as follows.

$$Re_m = \frac{U_{s,f} \times \text{Velocity scale} \times D_{s,f} \times \text{Length scale}}{\text{Kinematic viscosity of model source fluid}} = \frac{U_{s,f}}{30} \times \frac{D_{s,f}}{45} \times \frac{1}{\nu_{s,m}}$$

Taking a conservative value of 3 feet for the characteristic length dimension $D_{s,f}$

$$Re_{m,\text{ trough dumping}} \approx 2100$$

$$Re_{m,\text{ lancing}} \approx 1050$$

These values establish that the model plumes are well into the turbulent regime.

Time Scale and Filming Rate

The time scale of modeling is defined as the ratio of the average time of fume rise for the model to that of the full-scale system.

$$\text{Time scale} = \frac{\left[\dfrac{\text{height of roof monitor}}{\text{average fume rise velocity}}\right]_m}{\left[\dfrac{\text{height of roof monitor}}{\text{average fume rise velocity}}\right]_f} = \frac{\left[\dfrac{D_s}{U_s}\right]_m}{\left[\dfrac{D_s}{U_s}\right]_f} = \frac{1}{1.5}$$

This implies that, for corresponding events of the model and full-scale systems, fume rise velocities of the model would appear to be faster than those of the model plumes by a factor of 3 to 2. Therefore, for visual comparisons of the model and field movies, the model films should be projected at two-thirds of the speed at which they were shot. (In this study, model films were shot at 36 frames per second thereby requiring a projection speed of 24 frames per second for visual comparisons.)

TEST RESULTS

A summary of the model tests (which were also documented in a captioned movie film) is given in Table 2.

OBSERVATIONS REGARDING MODEL HOOD PERFORMANCE

A brief summary of the observations for each of the hoods in its different locations is given below (selected photographs taken during testing of the hoods are shown in Figures 6 and 7).

Low-level Hood, Offset From Bustle Pipe

This hood was intended for capture of lancing fumes. Even for the relatively high face velocity used, performance of this hood in the offset position is poor. Plume fluid excapes through the gap between the hood and the bustle pipe and also around the bottom of the bustle pipe.

Low-level Hood, Against the Bustle Pipe

In this position, hood collection is much better than in the offset position. Plume fluid reaching the immediate vicinity of the hood is captured whereas that hitting the bustle pipe and spreading out underneath it still escapes.

Small Hood at Truss Level, Located Close to Furnace

Performance of this hood for lancing is somewhat inferior to that of the low-level hood in the position against the bustle pipe. For the other events, large fractions of the major emissions miss the hood. However, emissions from the main trough are captured.

Small Hood at Truss Level, Offset From the Furnace

This hood, in the offset position, was not filmed for collection of lancing fumes as it was very ineffective in this case. During initiation of iron flow to the No. 1 ladle, most of the emissions from the No. 1 ladle and the runner leading to it are collected. However, emissions from the trough area close to the furnace are not collected. During dumping of the trough to the No. 1 ladle, a fair amount of the total emission is captured by the hood. However, spill-over at the edges of the hood can be observed, indicating that the hood area is insufficient to handle such large emission rates.

Large Hood at Truss Level

Performance of this hood during lancing is comparable to that of the small hood at truss level, when located close to the furnace. Both for initiation of iron flow to the No. 1 ladle and dumping of the trough to the No. 1 ladle, collection efficiency appears to be good. However, a tendency for the emissions to overflow the edges of the hood can be noticed at times. This observation, together with the fact that the plume fluid beneath the hood overflows and clouds the area in immediate response to the loss of hood

TABLE 2. SUMMARY OF MODEL TESTS

Test No.	Model Source Flow Rate gpm	Full-Scale Source Emission Rate acfm	Model Hood Flow Rate gpm	Full-Scale Hood Flow Rate & Face Velocity acfm : fpm
		LANCING TO OPEN NOTCH		
		• No Canopy Hood Collection		
1	0.5	4,000	0	0 : 0
		• Low-Level Hood Offset from Bustle Pipe		
2	0.5	4,000	6.5	52,000 : 308
		• Low-Level Hood Against Bustle Pipe		
3	0.5	4.000	6.5	52,000 : 308
		• Small Hood at Truss Level Located Close to Furnace		
4	0.5	4,000	18.4	147,200 : 229
		• Large Hood at Truss Level		
5	0.5	4,000	18.4	147,200 : 122
		IRON RUNNING TO NO. 1 LADLE		
		• No Canopy Hood Collection		
6	1.2	9,600	0	0 : 0
		• Small Hood at Truss Level Located Close to Furnace		
7	1.2	9,600	18.4	147,200 : 229
		• Small Hood at Truss Level Offset from Furnace		
8	1.2	9,600	18.4	147,200 : 229
		• Large Hood at Truss Level		
9	1.2	9,600	18.4	147,200 : 122
		TROUGH DUMPED TO NO. 1 LADLE		
		• No Canopy Hood Collection		
10	2.2	17,600	0	0 : 0
		• Small Hood at Truss Level Located Close to Furnace		
11	2.2	17,600	18.4	147,200 : 229
		• Small Hood at Truss Level Offset from Furnace		
12	2.2	17,600	18.4	147,200 : 229
		• Large Hood at Truss Level		
13	2.2	17,600	18.4	147,200 : 122

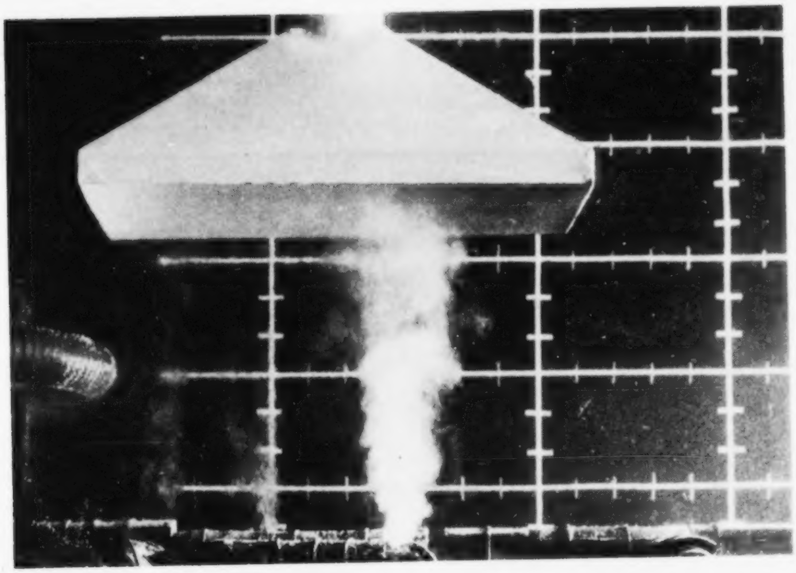

Figure 6. Large Hood at Truss Level, Iron Running to No. 1 Ladle
Simulated Hood Evacuation Rate: 147,000 acfm

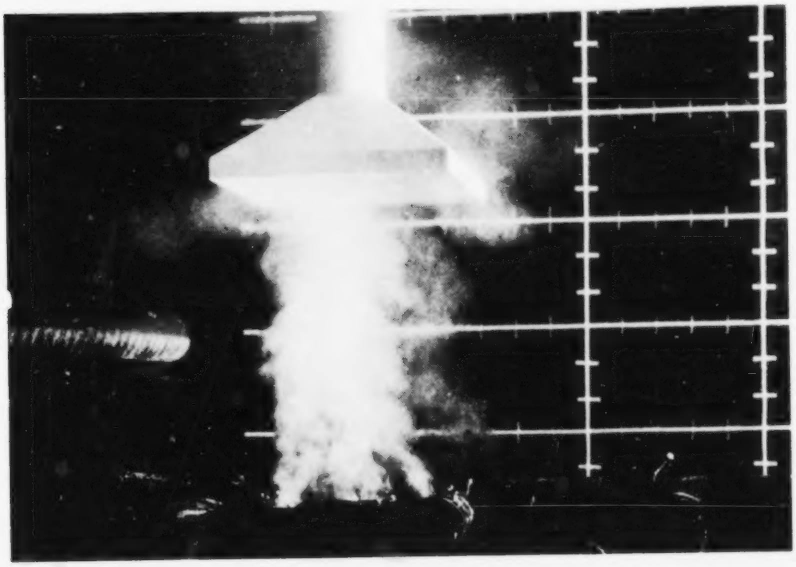

Figure 7. Small Hood at Truss Level, Trough Dumped to No. 1 Ladle
Simulated Hood Evacuation Rate: 147,000 acfm
Hood Offset from Furnace

evacuation, suggests that the hood plenum is probably filled to capacity in these cases and a somewhat higher evacuation rate would therefore be desirable.

CONCLUSIONS AND RECOMMENDATIONS

The two truss-level hoods were evacuated at the same volume flow rate (full-scale equivalent: 147,000 acfm) for purposes of comparison. Corresponding full-scale hood face velocities were 122 fpm for the larger hood and 229 fpm for the smaller. The larger hood, in spite of its lower face velocity, gave the most promising overall performance in terms of control of all emissions under consideration. The low-level hood at bustle-pipe level (for control of lancing and main trough emissions only) did not perform entirely satisfactorily for any of the cases tested and was found to be highly sensitive to horizontal positioning relative to the bustle pipe. However, it does offer the possibility of some control with a small hood and a small volume flow rate. Its performance could most likely be improved by the addition of hood skirting. In view of the severe restrictions on the dimensions and location of this hood, it was tested at the relatively high full-scale equivalent face velocity of 308 fpm (50,000 acfm). This value of the hood velocity was arrived at from a set of preliminary tests. The preliminary tests showed that the performance of this hood improved significantly when the hood face velocity was raised from about 180 fpm to 308 fpm (full-scale equivalent values). However, only marginal improvement was observed when the hood face velocity was further increased to the full-scale equivalent of 500 fpm. (In these model tests, the gap between the bustle pipe and the furnace wall was blocked off, thereby cutting off the passage of fumes through this area. This would be necessary in the full-scale situation to achieve reasonably efficient hood capture of lancing emissions and to a somewhat lesser extent emissions from the main trough.)

The modeling technique described in this study can be used to select optimal designs of hoods, their locations and evacuation rates. Although in the present series of tests only qualitative analysis of hood performance was done, the authors have formulated a test procedure to yield numerical values of hood efficiencies using the same test setup. This involves the additional determination of sodium sulphate concentration in the hood flow by chemical analysis. This data can then be used, in conjunction with the known values of source emission and hood volume flow rates and the sodium sulphate concentration in the source fluid (the surrounding fluid contains essentially no sodium sulphate), to determine numerical values for hood collection efficiencies, thus allowing a quantitative evaluation of hood performance. Chemical analysis of the fluid collected by the hood can be done either by the gravimetric method (separating and weighing) or by nephelometry (measurement of light scattering). Either method will yield sodium sulphate concentrations with accuracies sufficient to differentiate hood efficiency variations of less than 5%. With this capability, one can also accurately evaluate the effects on hood efficiency of other factors such as hood skirting and hood take-off configurations for a finer degree of system design optimization.

The present study did not take into account the effects of cross-drafts induced by winds. However, outside air infiltration patterns into the building under calm conditions were roughly simulated by incorporating openings in the cast house model. In cases, where significant cross-drafts are present, their effects on hood performance may also have to be evaluated by model tests before finalization of system design. This can be done by examining hood performance while recirculating the brine solution through wall openings in the model cast house at flow rates that scale the air volume flow rates through the full-scale openings.

The laboratory model has at this point been fully developed and sufficiently demonstrated in a sample application to justify its intended use in the evaluation of potential designs for hooding systems to control blast furnace casting emissions. In general, for each application the following steps would be required:

1) Site visit and selective filming of full-scale emissions.
2) Derivation of full-scale data by analysis of the film, shop drawings and other information.
3) Selection of scales and fabrication of model cast house.
4) Determination of potential full-scale hood dimensions and locations.
5) Design and fabrication of model hoods.
6) Calibration check of model system for proper simulation of emissions.
7) Performance of model tests to select optimal hood design, location and evacuation rate.
8) Evaluation of the effect of cross-drafts on hood performance and incorporation of design modifications if necessary.

ACKNOWLEDGEMENT

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Session 2: SOLID WASTE POLLUTION ABATEMENT

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RCRA REGULATORY CHANGES AND THE STEEL INDUSTRY

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ABSTRACT

The objectives of the Resource Conservation and Recovery Act (RCRA) in the management of solid and hazardous wastes are to promote the protection of human health and the environment and to conserve valuable material and energy resources. This paper presents an update of the actions being taken by the Environmental Protection Agency (EPA) in fulfilling the objectives of RCRA with respect to hazardous waste management. It discusses: (1) the status of regulations promulgated to manage hazardous wastes, and (2) RCRA activities specifically associated with steel industry hazardous wastes.

Standards were published in May 1980, establishing a foundation for the management of hazardous waste, and additional technical standards necessary to permit treatment, storage, and disposal facilities were published in January and February 1981.

However, some wastes listed as hazardous in May of 1980 have subsequently been delisted, and the effective dates of some of the January and February standards have been deferred.

EPA has also been involved in the investigation of means to alleviate the problem of spent pickle liquor generated by the steel industry via increased reuse/recovery. With regard to the latter, EPA has recently promulgated a conditional exemption from RCRA management standards for spent pickle liquor use and is also currently considering a Section 6002 procurement guideline for the specific use of spent pickle liquor in wastewater treatment as a phosphorous removal agent.

An overview of each of these EPA activities under RCRA is provided in this paper.

RCRA AND THE STEEL INDUSTRY

The objectives of the Resource Conservation and Recovery Act (RCRA) in the management of solid and hazardous wastes are to promote the protection of human health and the environment and to conserve valuable material and energy resources. This paper presents an update of the actions being taken by the Environmental Protection Agency (EPA) in fulfilling the objectives of RCRA with respect to hazardous waste management. It discusses: (1) the status of regulations promulgated to manage hazardous wastes, and (2) RCRA activities specifically associated with steel industry hazardous wastes.

Structure of Subtitle C

Under Subtitle C of RCRA, EPA is required to establish a Federal hazardous waste management system that involves "cradle-to-grave" control of hazardous waste. Section 3001 of Subtitle C defines criteria for the identification and listing of hazardous waste. Section 3002 and 3003 mandate standards for generators and transporters, including a manifest system which is designed to track the movement of hazardous waste from generators through transporters to hazardous waste treatment storage and disposal facilities. Section 3004 specifies that owners and operators of treatment, storage and disposal facilities comply with standards that "may be necessary to protect human health and the environment." All standards become effective six months after their promulgation. Subtitle C requires in Section 3005 that these standards be implemented through permits, issued by EPA or authorized states. Recognizing that not all permits would be issued within six months of promulgation of the Section 3004 standards, Congress created "interim status" in Section 3005(e) of RCRA. Owners and operators of hazardous waste treatment, storage, and disposal facilities who qualify for interim status will be treated as having been issued a permit until EPA takes final administrative action on their permit application. Finally, Section 3006 requires that the Agency establish guidelines for authorizing states to carry out the RCRA Subtitle C program.

The Subtitle C mandates and associated regulatory subjects are summarized below.

RCRA Section	Regulations in CFR	Subject of Regulation
3001	Part 261	Identification and Listing of Hazardous Wastes
3002	Part 262	Standards for Generators of Hazardous Wastes
3003	Part 263	Standards for Transportation of Hazardous Wastes
3004	Part 264, 265, 266, and 267	Standards for Owners and Operators of Hazardous Waste - Treatment, Storage, and Disposal Facilities
3005	Part 122 124, 125	Permits for Treatment, Storage, and Disposal of Hazardous Waste; Consolidated Permits
3006	Part 123	Guidelines for Authorized State Hazardous Waste Program
3010	-----	Preliminary Notification of Hazardous Waste Activity

Status of Subtitle C Rulemaking

In May of 1981 the Agency published Phase I of the Subtitle C regulations. The Phase I regulations included: identification and listing of hazardous waste (Part 261); a manifest system and other standards for generators and transporters; (Parts 262 and 263); interim status standards and some general administrative standards for treatment, storage and disposal facilities (Part 264 and 265); permitting procedures (Parts 122 & 124); and guidelines for authorized state hazardous waste programs (Part 123). The Phase I regulations established the foundation of the RCRA Subtitle C regulatory program. However, they did not include the important technical standards necessary to permit treatment, storage and disposal facilities.

The latter standards, representing Phase II of the Subtitle C regulatory program, were published in January and February of this year. They are known as general standards and are codified in Parts 264 and 267. These regulations are all currently undergoing an intensive regulatory review and consequently the effective dates of some of these standards have been deferred. More specifically, the status of the Phase II standards is as shown in Table 1.

The status presented in Table 1 is a general, rather than a detailed or legal, statement of the status of the regulations, and is intended only as a general reference. It does not include roughly a dozen technical amendments which have clarified or modified certain parts of the regulations. It also does not include response to petitions for "delisting" wastes, and it does not reflect the aspects of these regulations which have been challenged in litigation proceedings, and which therefore could undergo change through negotiated settlements or court action.

In addition to the regulatory development and review efforts, the Agency is moving as rapidly as possible to authorize States to assume the RCRA regulatory program. To date, 25 States have been authorized for Phase I of the RCRA program.

Specific RCRA Activities Affecting the Iron and Steel Industry

Since the publication of the initial hazardous waste management regulations under RCRA in May 1980, the Agency has been involved in at least two activities related to steel industry hazardous wastes:

1) the ongoing review of the need to list or delist specific steel industry waste streams

TABLE 1

Status of Phase II RCRA Regulations

Type of Facilities	Date Published	Effective Date
Storage and treatment in containers, tanks, and piles (Part 264; Subparts I, J, L)	Jan. 12, 1981	July 13, 1981
Incinerators (Part 264; Subpart O)	Jan. 23, 1981	July 22, 1981- (New Facilities) July 22, 1981 (Existing Facilities) [1]
Storage and Treatment in surface impoundments (Part 264; Subpart K)	Jan. 12, 1981	July 13, 1981 (New Facilities) July 13, 1981 (Existing Facilities) [1]
Land disposal in landfills, surface impoundments, and underground injection wells; land treatment; groundwater monitoring (Part 267)	Feb. 13, 1981	Aug. 13, 1981 [2]
Financial requirements (Part 264; Subpart H)	Jan. 12, 1981	April 13, 1982 [3]
Closure & Post Closure Plans	May 19, 1981	May 19, 1982

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[1] On July 24, 1981 the Agency announced its intention to initiate rulemaking to suspend the effective date of these standards pending further evaluation of their appropriateness for existing facilities.

[2] These standards apply to new facilities only.

[3] The Agency announced in the Federal Register on September 30, 1981 a deferral of the effective date from October 13, 1981 to April 13, 1982.

2) the investigation of means by which to alleviate the problem of spent pickle liquor disposal via increased reuse/recovery

A. Steel Industry Hazardous Wastes Listing

In the May 19, and July 16, 1980 Federal Registers, six wastes associated with the steel industry were listed as hazardous wastes by EPA. The six specific wastes listed and their hazardous characteristic(s) are:

1) Ammonia still lime sludge from coking operations, (toxicity);
2) Decanter tank tar sludge from coking operations, (toxicity);
3) Emission control dust/sludge from the primary production of steel in electric furnaces, (toxicity);
4) Sludge from the lime treatment of spent pickle liquor from steel finishing operations, (toxicity);
5) Spent pickle liquor from steel finishing operations, (corrosivity, toxicity).
6) Dewatered Air Pollution Control Scrubber Sludges from Coke Ovens and Blast Furnaces, (toxicity).

A number of other wastes (from non-specific sources) which may be associated with some steel industry operations were also listed as hazardous. These include such wastes as spent halogenated and non-hologenated solvents, still bottoms from the recovery of these solvents, and various sludges generated from metal heat treating and electroplating operations.

Based on further investigation of the characteristics of these wastes and review of comments submitted regarding their hazardous waste listing, EPA has made the following revisions to the original listing of hazardous wastes associated with the steel industry:

- "Sludge from lime treatment of Spent Pickle Liquor from Steel Finishing Operation - (K063)

EPA has decided to revise the regulatory approach for this waste by deleting it from the hazardous waste list but still regulating it as hazardous since it is generated from the treatment of another listed hazardous waste - spent pickle liquor - (K062). Delisting petitions will be considered when it can be demonstrated that the concentration of lead and chromium in EP extracts are significantly less than the maximum concentration levels of 100 X Interim Primary Drinking Water Standards. The Agency is also in the process of evaluating the feasibility of an industry-wide delisting petition for the waste submitted by the American Iron and Steel Institute.

- Spent Pickle Liquor from Steel Finishing Operations (K062)

EPA has exempted from the hazardous waste **regulations any spent pickle** liquor which is intended for use in NPDES permitted wastewater treatment facilities. Notice of this exemption appeared in the Federal Register of September 8, 1981. Aside from this specific use of spent pickle liquor, the disposal of this waste remains subject to the hazardous waste regulations.

- Spent Non-Halogenated Solvents (F005)

In the listing of spent non-halogenated solvents and still bottoms from the recovery of these solvents, the solvents methanol and methyl isobutyl ketone were listed due to both toxic and ignitable characteristics. Based upon further review, the Agency is no longer listing either solvent as a toxic waste, although both will continue to be listed as ignitable wastes under Hazardous Waste No. F003 since both are highly ignitable.

- Wastewater Treatment Sludges from Electroplating Operations (F006)

EPA has received comments suggesting that a number of these processes would not generate a hazardous waste because hazardous constituents, such as cadmium, chromium, cyanides, and nickel, are not used, and thus would not be expected to be present in the treatment sludges. Accepting these arguments, the Agency has modified the listing to exclude wastes generated by several electroplating processes, including:

1) tin plating on carbon steel
2) zinc plating (segregated basis) on carbon steel
3) aluminum or zinc-aluminum plating on carbon steel
4) all cleaning/stripping associated with tin, zinc, and aluminum plating on carbon steel

- Emission Control Dust/Sludge from Electric Furnace Steel Production (K061)

Due to some confusion as to the applicability of this listing, EPA affirmed that the intent of the listing was to include only wastes from primary steel production. Foundry electric furnace emission control dusts and sludges are not included in this specific listing but are being evaluated separately.

- Dewatered Air Pollution Control Scrubber Sludges from Coke Ovens and Blast Furnaces (F016)

After assessing comments, the Agency believes that it overestimated the amount and migratory potential of complexed cyanides in these wastes. Consequently, this waste has been deleted from the hazardous waste list.

In addition to the above mentioned changes to the listings of steel industry hazardous waste, EPA is also currently undertaking a study to comprehensively assess the characteristics of wastes associated with coke-making processes. This study will enable EPA to determine the hazardousness of these waste streams.

B. Promotion of Spent Pickle Liquor Recovery/Reuse

One of the goals of RCRA is to increase resource recovery and conservation. Therefore, in addition to assuring environmentally sound management practices for the disposal of solid wastes, it is also EPA's intent to promote the recovery/reuse of solid waste.

We believe that the environmentally safe recovery and reuse of spent pickle liquor has been demonstrated and will be feasible in numerous situations. Specifically, in many cases the use of spent pickle liquor in wastewater treatment operations for the removal of phosphorous represents an acceptable waste management technique.

Although almost 1 billion gallons of spent pickle liquor are generated each year, only perhaps 5% - 10% of this amount is reused or recovered for this use. The reasons for this low recovery rate include: (1) previously inexpensive disposal options, (2) the difficulty of marketing a waste product, (3) unwillingness of many wastewater treatment plant operators to try a new product, (4) inability of municipalities to enter into long term contracts, and (5) only relatively recent stringent requirements for phosphorous removal.

The treatment and disposal of spent pickle liquor has always been a problem for the steel industry. In the past, various dumping alternatives allowed for a relatively low cost means of spent pickle liquor disposal. As a result, development and utilization of recovery and reuse techniques have not been strongly pursued. Common methods for management of the spent pickle liquor included: untreated disposal (61%), on-site neutralization (21%), contract hauler (11%), reuse or recovery (7%). Untreated disposal includes (1) direct discharge into waterways, (2) deep well injection, and (3) disposal on a slag pile or similar dumping. Under RCRA, these untreated disposal practices will be virtually halted, thereby necessitating the development of an acceptable alternate management option for the disposal of a major portion of spent pickle liquor generated.

Neutralization, although costly, may provide a cost effective short term alternative. Although acid recovery (in which the dissolved iron salts are removed from the spent acid, which can then be reused) has been shown to be the most favorable spent pickle liquor management alternative based on resource recovery and environmental protection goals, its implementation has been held back by the relatively large capital costs needed to construct recovery facilities. This impediment should gradually be alleviated as a result of continuing development of less expensive acid recovery units adaptable to a wide range of pickling facilities.

Due to regulatory requirements for the disposal of hazardous wastes, it is expected that the cost of disposing of spent pickle liquor will increase significantly not only due to additional treatment requirements but also to the decreasing number of acceptable disposal sites. Until such time that acid recovery techniques are wholly feasible, EPA believes that the direct use of spent pickle liquor for phosphorous removal in wastewater treatment facilities will serve to:

(a) provide an effective, inexpensive alternative phosphorous removal agent;

(b) serve as an appropriate waste management technique for spent pickle liquor; and

(c) assist in the conservation of our natural resources by reducing the need for those raw materials used in or as commercial chemicals for phosphorous removal purposes.

Spent Pickle Liquor for Phosphorous Removal

The removal of phosphorous from wastewaters is considered essential for the control of eutrophication* and the prevention of water quality deterioration in many receiving streams. Perhaps the most outstanding example of this need for phosphorous control is the Great Lakes Region where the discharge of phosphorous into Lakes, is or will be, restricted to 0.5 to 1.0 milligrams per liter in order to preclude further deterioration of the waterways and hopefully reverse the eutrophication condition.

Of the methods available for phosphorous removal, chemical precipitation (coagulation) using aluminum, ferric iron, ferrous iron, and lime is considered to be the most effective and economical. These chemical precipitation methods depend on the use of soluble salts of the metal to coagulate the phosphorous. Iron, both ferrous and ferric, and aluminum are employed as the sulfate and chloride salts. Spent pickle liquor, has the iron for phosphorous removal present as ferrous sulfate or ferrous chloride (depending on whether the pickling operation uses sulfuric or hydrochloric acid). This being the case, spent pickle liquor can in many cases substitute for commercial chemicals.

Examples of the successful use of spent pickle liquor include its applications in the wastewater treatment facilities at Washington, DC, Baltimore, Milwaukee, Detroit, and Roanoke, VA. These examples of spent pickle liquor use in wastewater treatment facilities are but a sampling of similar applications which demonstrate the effectiveness of waste pickle liquor in removing phosphorous in municipal wastewater treatment facilities that have traditionally utilized higher-priced commercial chemicals for that purpose.

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* Eutrophication designates that state of a body of water in which the increase of mineral and organic nutrients has reduced the dissolved oxygen, thereby resulting in an environment that favors plant over animal life.

The feasibility of increased utilization of spent pickle liquor led the Agency to initiate two specific actions to foster its increased use. One of these actions is a conditional exemption for spent pickle liquor from the management standards that apply to hazardous wastes. This exemption applies to facilities which reuse spent pickle liquor, to generators and brokers who accumulate spent pickle liquor, and to those who transport spent pickle liquor, where the spent pickle liquor is to be reused in wastewater treatment at a facility holding a National Pollution Discharge Elimination System (NPDES) permit.

The Subtitle C regulations previously exempted the actual reuse application from regulation, because all ligitimate reuse and recovery facilities were exempted in Section 261.6 of the regulations. However, for listed wastes, such as spent pickle liquor, a manifest and other generator and transporter standards applied, and the storage at the reuse facility was regulated. This discouraged the use of spent pickle liquor because wastewater treatment facilities were reluctant to be publically identified as a hazardous waste management facility. The exemption removes all of these standards.

EPA believes that this exemption will not pose a substantial hazard to human health or the environment because in this specific use of spent pickle liquor the objectives of the hazardous waste regulations appear to be achieved by current in-place controls. For instance, the spent pickle liquor must be shipped in compliance with Department of Transportation hazardous materials regulations, and when received by the user facility, will be stored in tanks comparable to those in which similarly corrosive commercial chemicals (ferric chloride, alum) are kept.

In making the exemption, the Agency will thus reduce the regulatory burden to those individuals who reuse spent pickle liquor in wastewater treatment, encouraging its use, but without increasing the risk of harm to human health and the environment.

In addition to making an exemption from the hazardous waste regulations for that spent pickle liquor which is utilized at NPDES permitted wastewater treatment facilities, EPA is also specifically promoting the increased use of spent pickle liquor in such facilities as a phosphorous removing agent. The particular avenue within RCRA for promoting this increased use of spent pickle liquor is RCRA Section 6002.

Section 6002 of the Solid Waste Disposal Act, as amended by RCRA, 42 U.S.C. 6962, requires Federal, State, and local procuring agencies, using appropriated Federal funds, to purchase items composed of the highest percentage of recovered materials practicable, given that reasonable levels of competition, cost, availability, and technical performance are maintained. EPA is required to prepare guidelines to assist procuring agencies in complying with the requirements of Section 6002.

Although the potential for use of spent pickle liquor is somewhat limited at Federal facilities, EPA believes that its use at these facilities would offer a cost savings to the government with respect to the purchasing of treatment chemicals, and would additionally provide increased opportunities for demonstration of the effectiveness of spent pickle liquor for phosphorous removal. Hopefully, a "spinoff effect" of this spent pickle liquor utilization will be an increased awareness and willingness on the part of non-Federal wastewater treatment facility operators to consider the use of spent pickle liquor for phosphorous removal.

A RCRA Section 6002 guideline would designate spent pickle liquor used in wastewater treatment operations for phosphorous removal as a product for which procuring agencies must exercise affirmative procurement under Section 6002 of RCRA and presents recommendations for carrying out the requirements of Section 6002 regarding the use of spent pickle liquor in wastewater treatment operations.

The requirements of Section 6002 apply to "procuring agencies". The term "procuring agency" is defined in RCRA as "any Federal agency, or any State agency or agency of a political subdivision of a State which is using appropriated Federal funds for such procurement, or any person contracting with any such agency with respect to work performed under such contract".

One approach being considered for the guideline is to recommend that any purchases of chemicals for phosphorous removal made with Federal funds, either directly or indirectly, allow for spent pickle liquor to be bid as an alternate material, unless it can be shown that the use of spent pickle liquor is technically inappropriate for a particular wastewater treatment application.

Whatever approach is chosen, it is EPA's hope that it would assist in achieving a significant increase in the reuse and recovery of spent pickle liquor, thus lessening the environmental and economic burdens its disposal now poses.

CHARACTERIZATION, RECOVERY AND RECYCLING OF ELECTRIC ARC FURNACE DUST

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ABSTRACT

Electric arc furnace dust samples have been obtained from a number of steel companies chosen to represent the broad spectrum of steelmaking practice. The samples have been chemically and structurally analyzed in the bulk and individual particles have been characterized using analytical electron microscopy techniques.* Procedures to extract elements from the dust have been investigated by both physical and chemical methods. Magnetic separation procedures show some promise for recovering zinc from high zinc bearing dust. Other options for resource recovery are discussed including the technologies which exist for processing high grade dust.

INTRODUCTION

Dusts and fumes from steelmaking in electric arc furnaces contain impurities that are undesirable for recycling by the normal methods. The major undesirable elements in the dust are zinc, lead, sulfur, phosphorus, sodium, potassium and their compounds. Recycling or disposal of electric arc furnace dust is further complicated by the fact that the dust is extremely fine and difficult to handle. Moreover, the problem of disposal became more acute when the dusts were declared a hazardous waste. Poor characterization of electric furnace dust in the past has made the selection of recovery, recycling or disposal options difficult. In addition the high cost of disposal has generated new interest in methods for recovery or recycling.

The U.S. Department of Commerce through the Economic Development Administration has provided a grant to Lehigh University to characterize electric-arc furnace dusts, reviewing the recovery/disposal options, and to estimate the available resources represented in these dusts. This paper presents some of the findings of the Lehigh study.

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* Most particles analyzed were complex iron rich spinel oxides with varying amounts of other elements in solid solution.

CHARACTERIZATION OF ELECTRIC FURNACE DUSTS

INTRODUCTION

Thirty-three samples of electric-arc furnace dust were supplied by twenty-five steel plants representing a wide variety of steel products. The dust samples were carefully homogenized and split. Bulk chemical analyses including the EP Toxicity Test were undertaken by the U.S. Bureau of Mines, Avondale Research Center. The electron microscopy characterization of individual particles of dust, by size and chemistry was undertaken at Lehigh University. In addition x-ray diffraction and Mössbauer spectroscopy techniques were used to establish the mineralogy of the samples.

One large representative sample of carbon steel dust and one large representative sample of stainless steel dust were given a series of chemical dissolution or leaching tests by the U.S. Bureau of Mines, Rolla Research Center, and physical separation tests by the U.S. Bureau of Mines, Twin Cities Research Center.

Dust from stainless and high alloy steels differs from carbon steel dust. Thus each type of dust represents a different set of problems relative to the disposal and recovery options. Table 1 illustrates the differences in bulk chemistry. As expected the alloying elements chromium, nickel and molybdenum show up prominently in the stainless steel and specialty alloy dust. The amounts of these elements are sufficient to make recovery a viable activity. The copper level is high in the alloy dust because monel type alloys are produced in one of the selected furnaces. Cadmium is observed in large amounts as a result of reclaiming nickel from nickel-cadmium batteries. High fluorine contents probably result from greater use of spar for slag conditioning. Carbon steel dusts are richer in zinc and lead because of the greater use of galvanized and other coated products in the melt. The quantities of zinc involved in electric furnace dust, if recoverable, would represent a significant increase in the United States resources of zinc.

Most of the dusts failed the EP leachate toxicity tests primarily because of the high levels of cadmium, lead and hexavalent chromium. However only stainless and high alloy steel dust contained excessive hexavalent chromium. In general the cadmium and lead were highest when the amount of purchased steel scrap was high. In the case of cadmium, 40 to 100 percent of the cadmium in the dust was found in the leachant. For lead only 2 to 17 percent was transferred to the leachant. When chromium was present in significant amounts, a relatively small percentage ended up in the leachant, although the amount still exceeded the specified limits.

MINERAL COMPOSITION

Temperatures near the electric arc are sufficiently high to vaporize various constituents of the charge including both volatile and non-volatile metals. The processes of vaporization, condensation and oxidation gives rise to the formation of complex fumes. The dominant mineral phases in all samples are oxides with the spinel structure and lattice parameters indicating compositions close to magnetite (Fe_3O_4) or zinc ferrite ($ZnFe_2O_4$). Individual

TABLE 1. CHEMICAL COMPOSITION OF DUST FROM ELECTRIC FURNACES

Carbon and Low-Alloy Steels			Stainless Steel and Specialty Alloys		
Element	wt%*	Range %	Element	wt%**	Range %
Al	0.25	0.09-0.53	Al	0.40	0.20-0.60
Ca	4.19	1.85-10.0	Ca	3.91	1.76-6.93
Cd	0.05	0.03-0.15	Cd	0.46	0.006-1.79
Cr	0.22	0.06-0.58	Cr	5.88	2.01-10.1
Cu	0.23	0.06-0.32	Cu	0.62	0.09-1.26
K	0.66	0.06-1.12	K	2.07	0.80-5.07
Mg	1.68	0.77-2.93	Mg	3.78	1.70-4.74
Mn	3.29	2.46-4.60	Mn	3.72	2.36-4.59
Mo	0.02	<0.02-0.08	Mo	1.08	0.37-1.46
Na	0.99	0.29-2.31	Na	2.12	0.47-4.60
Ni	0.04	0.01-0.12	Ni	1.69	0.15-3.34
Pb	2.02	1.09-3.81	Pb	0.52	0.23-0.78
Zn	18.3	11.12-26.9	Zn	4.58	1.77-6.22
Fe^{Total}	31.3	24.9-46.9	Fe^{Total}	27.0	22.2-35.5
Fe^{+3}	29.7	20.5-42.8	Fe^{+2}	4.47	0.53-5.90
Fe^{+2}	1.46	<0.01-3.96	Cr^{+6}	0.10	<0.01-0.17
Fe^{0}	0.09	<0.02-0.34	Si	3.38	2.54-3.92
Cr^{+6}	<0.01	<0.01-0.02	Cl	0.81	0.47-1.17
Si	1.81	1.35-2.49	F	2.48	1.36-4.83
Cl	1.11	0.51-2.36	P	0.02	0.01-0.04
F	0.41	0.01-0.88			
P	0.03	0.01-0.08			

*arithmetic averages of dust from seven plants.
**arithmetic averages of dust from four plants.

particle characterization, however, demonstrated that many elements can substitute for the iron or zinc, in particular manganese and chromium.

Calcium oxide was present as free oxide in many of the bulk dust samples. Zinc oxide was present in samples containing large amounts of zinc. In all cases zinc is present in the spinel phase. Small amounts of hematite (α-Fe_2O_3) were found in most samples. An expanded lattice parameter and microanalysis indicated the presence of manganese in the hematite structure. Lead compounds were not observed by x-ray diffraction but lead-rich particles were seen in the SEM and TEM. Dissolution studies indicate that lead is present primarily as the oxide and secondarily as a silicate and that cadmium was probably present as an oxide.

The presence of calcium difluoride, potassium chloride and sodium chloride was indicated by x-ray diffraction. Minor amounts of metallic iron and possibly magnesium oxide were also observed in most samples. In addition small amounts of several unidentified structures were noted. Possibly these unidentified structures were complex silicates. Minor amounts of graphite were detected in most samples. Those samples having the most intense graphite peaks also had a higher free carbon content as shown by chemical analysis. The graphite particles were probably blasted from the graphite electrodes by the arc and may have some role in the nucleation of fume.

PARTICLE CHARACTERIZATION

Individual particles of dust from all the thirty-three samples have been examined using a scanning electron microscope (SEM) equipped with energy dispersive x-ray analysis (EDS). In addition fractions of the dust, size separated by centrifugation techniques and magnetically separated have also been prepared and examined. The technique allows the size and shape of individual particles to be correlated with the chemical elements present in the dust, with the restriction that low atomic number elements cannot be detected. A further restriction is that sodium in the presence of zinc cannot be detected and sulfur, molybdenum and lead have overlapping x-ray peaks. Specimens were prepared for scanning electron microscopy by ultrasonic dispersal in isopropyl alcohol followed by deposition on (0.2 μm pore size) nuclepore filters. The filters were viewed directly after carbon deposition. For transmission electron microscopy (TEM), the filter material was dissolved in chloroform, leaving the dust particles attached to a carbon film. More detailed studies have been performed on a small number of the samples using a scanning electron microscope with an automatic image analysis system* and a scanning transmission electron microscope (STEM) which allows for more accurate chemical analysis.

A typical specimen of dust particles is shown in Figure 1. Chemical analysis of individual particles by EDS showed most particles to be very similar with iron being the major detectable constituent with lesser amounts of manganese and calcium present. A few particles contained traces of sili-

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* The authors wish to acknowledge the assistance of R. Lee of U.S. Steel Research Labs in performing this work.

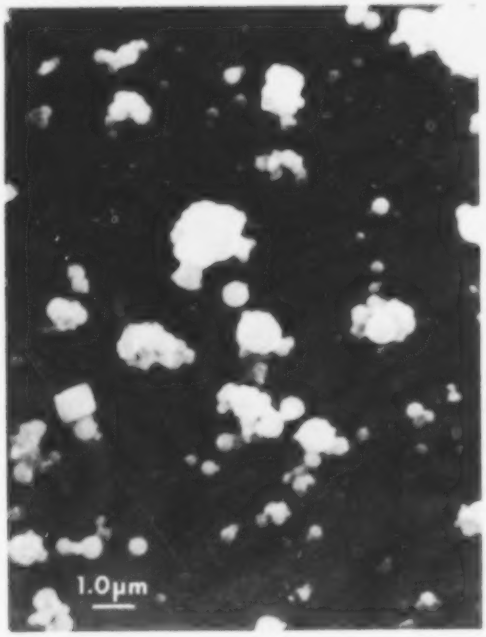

Figure 1: Dust particles supported on nuclepore filter for analysis.

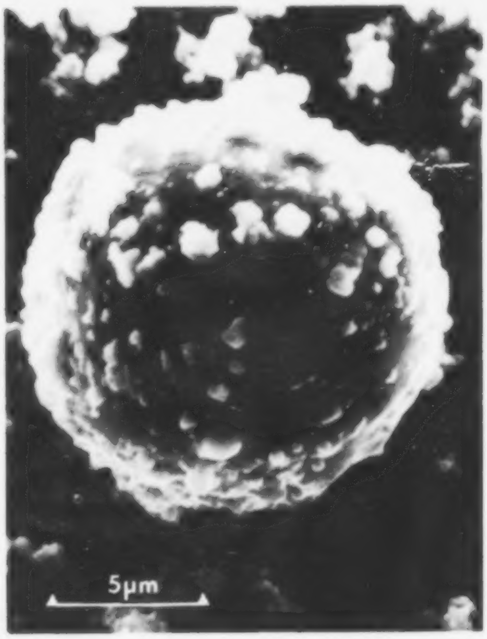

Figure 2: Large particle with outer shell iron rich.

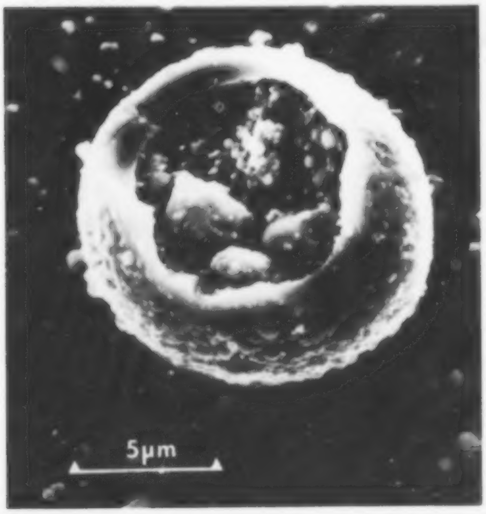

Figure 3: Broken shell of large particle revealing inner structure.

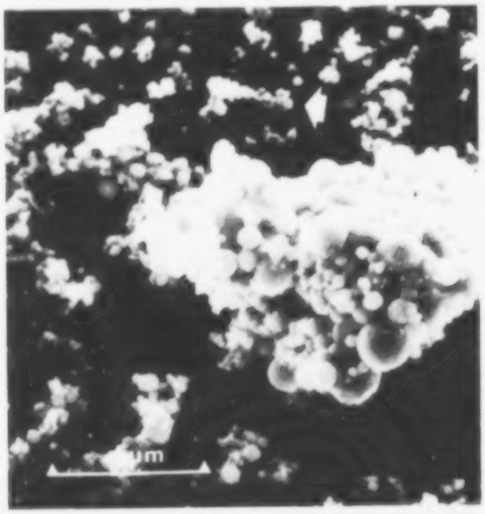

Figure 4: Agglomerated dust particles. A linear agglomerate is arrowed.

con and zinc. Of the particles analyzed, only one (arrowed) differed and that particle was calcium rich, with iron a strong secondary peak. The bulk chemical analysis for this sample showed only calcium (8.9%), manganese (5.3%) and zinc (2.9%) to be present above the 2% level. No measurements were made for silicon. X-ray diffraction of the bulk dust sample showed the major phase to be spinel with a lattice parameter consistent with magnetite having zinc and manganese substituting for iron. Microanalysis of small submicron particles confirmed that zinc and manganese were dissolved in the spinel lattice.

Individual particles tend to be in the range of 0.1 μm to 1 μm. Occasionally larger particles are observed, as in Figure 2, which shows a particle 11 μm in diameter, with smaller, sub-micron, particles attached to it. Only the presence of Fe was detected for this particle. The number of very large particles is small; however they may well constitute a major fraction of the dust by weight. One explanation for the formation of such large particles is that after initial formation, smaller particles agglomerate. If these particles are not swept out of the region of the furnace, further material is deposited onto them during the melt. There is evidence to suggest that volatile elements, such as zinc, are incorporated into the dust early in a melt and that later on a higher proportion of the dust is iron. One explanation for the high iron content of the large particle is that the outer layer which was analyzed was not deposited until near the end of the melt cycle.

The internal structure of one such large particle is shown in Figure 3. Microanalysis of the outer shell indicated iron with a subordinate, but high chromium peak. Analysis of several internal particles showed some to be iron rich, some calcium rich and some silicon rich. Only a small number of the analyzed samples contained such large particles. No correlation is observed between electric furnace dusts which contain large particles and the type of steel produced, scrap used, and/or furnace size or dust collection system.

A number of particle agglomerates are shown in Figure 4. Typically, agglomerates are made up of submicron particles, which, in general are spherical, although faceted particles are also frequently observed. The smaller agglomerates are often linear and presumably the particles are magnetically aligned. Some examples of linear agglomerates of particles are shown, arrowed in Figure 4.

A TEM photograph is given in Figure 5 and shows that some of the spherical particles have internal faceted crystalline cores. Other faceted particles are also observed and electron diffraction techniques show these to be spinel particles. Each of the particles in Figure 6, from a stainless steel furnace, are chrome rich and contain a subordinate amount of iron. Also present at lower levels were magnesium, zinc and silicon with trace amounts of vanadium, aluminum, manganese, calcium, copper, nickel and potassium. One of the major results of the microanalysis experiments is that a large number of elements are present in individual dust particles. In many cases these elements are present within a single spinel phase.

In many dust samples zinc oxide particles are very small and faceted, indicating formation by homogeneous nucleation from the vapor (see Figure 7). Typically such particles have up to 15% zinc substituted by such elements as

Figure 5: TEM image revealing internal structure of particles.

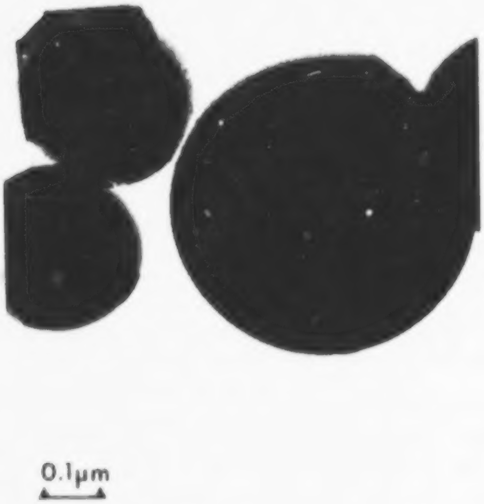

Figure 6: Faceted crystalline region within particle.

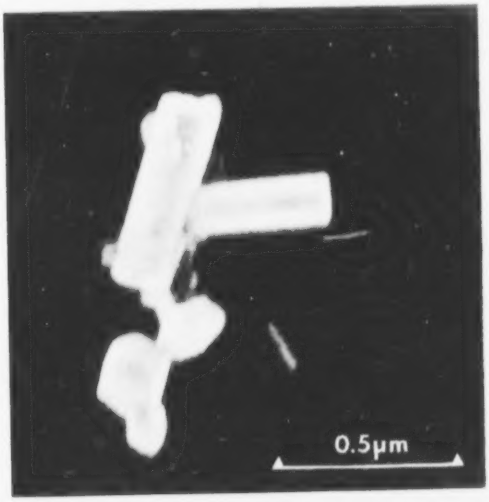

Figure 7: Faceted zinc oxide particles.

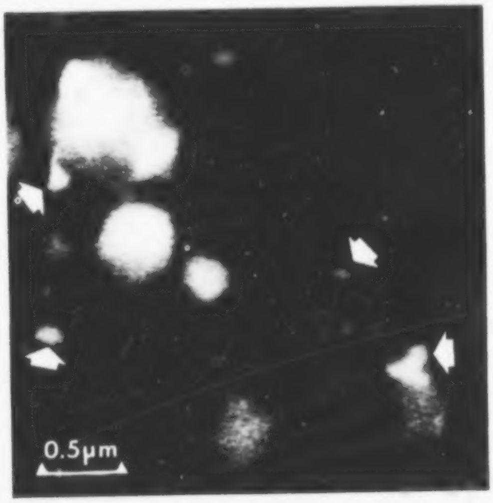

Figure 8: Backscattered image. Light regions, arrowed, are lead rich.

iron, aluminum, chromium, copper, nickel and possibly silicon. Often, the zinc oxide particles were part of a larger agglomerate, but still identifiable by diffraction and x-ray microanalysis. Some of the zinc oxide, however, formed into larger spherical particles, indistinguishable visually from the spinel and calcium rich particles. Lead, like zinc, often occurs in small particles within an agglomerate, or as small regions within a larger particle. Backscattered electron images can be used to pinpoint lead within an agglomerate (see Figure 8). The lighter regions in the figure are high atomic number and are lead-rich.

Dust samples can be characterized by grouping together those individual particles with the same one or two elements dominant in the EDS spectrum. Figure 9 shows such a characterization for two of the dust samples, Figure 9a representing a carbon steel dust and 9b a stainless steel dust. Each particle was assigned to one of the six classes or an unassigned class. For particles assigned to a single element class, the x-ray intensity detected for the major element in the particle had to be greater than 2½ times the intensity of any other element. To be assigned to a two element class, the second most intense x-ray peak observed had to exceed 40% of the intensity of the major peak.

Particles in the single element, iron class could be from either the magnetite or hematite phase. However, it is expected that hematite particles would fall into this class, since the solubility of other elements in hematite is small. Particles in the single element zinc class were shown to be zinc oxide and usually, only very low levels of solvent elements are detected in such particles. The number of particles assigned to the single element zinc class is probably too low, because the zinc oxide particles are often too small to generate adequate x-ray peaks in the SEM. Their presence was demonstrated more convincingly by STEM analysis.

The major difference in particle character between a carbon steel dust and a stainless steel dust is in the two element categories. The carbon steel dust had a large number of iron-zinc containing particles whereas the stainless steel dust revealed iron-silicon, iron-manganese and iron-chromium associations. The iron-zinc particles are presumably spinel phase close to zinc ferrite composition. Iron-manganese and iron-chromium could be either the spinel phase or hematite phase, and probably both exist. The structure of particles containing iron and silicon is complex and undetermined. In all cases minor amounts of other elements exist in the particles. For example, a typical particle in the iron-zinc category of the sample represented in Figure 9a could also contain lesser amounts of manganese, calcium, silicon and aluminum. Similarly, a particle assigned to the iron-chromium category in Figure 9b could also show the presence of manganese, silicon, magnesium and nickel. For both samples, the majority of the unassigned particles were calcium rich, with some silicon rich and magnesium rich particles included.

The SEM automated image analysis technique was a valuable complement to the characterization procedure since many particles could be analyzed in a short time, with the restriction that agglomerates were, in general, recognized as single particles.(1) The results from one such analysis are shown in Figure 10, for a carbon steel dust sample. The results are similar to

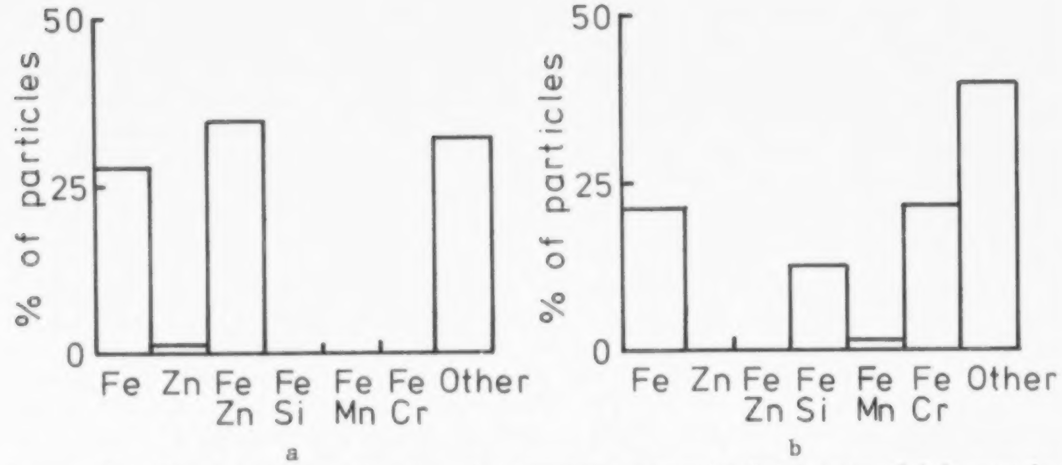

Figure 9: Histogram of classes of elemental associations into which particles fall. a) from a carbon steel dust, b) from a stainless steel dust.

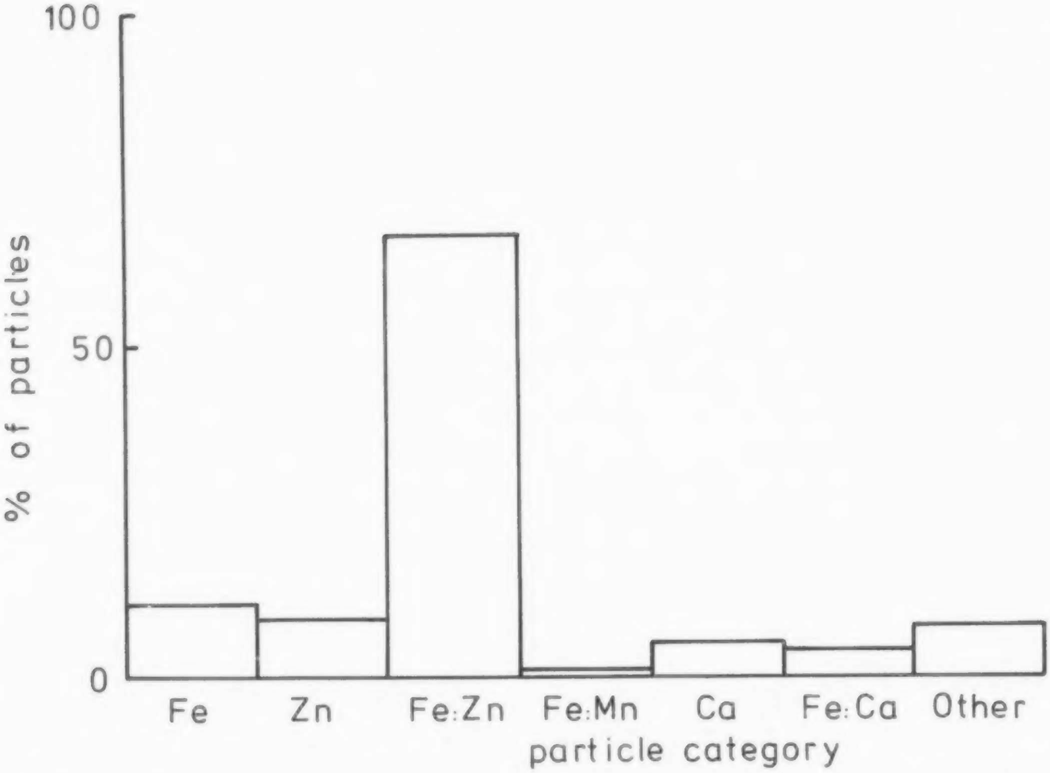

Figure 10: Histogram of classes of elemental associations for particles in a carbon steel dust: results are from SEM automated image analysis.

Figure 9a, although a larger percentage of particles exist in the iron-zinc category.

MAGNETIC SEPARATION STUDIES

The principle phases[*] present in the dust, classified according to their magnetic character,[**] are shown in Table 2. This table indicates that magnetic separation can, in principle, separate the dust into two categories; a non-magnetic zinc rich fraction suitable for economic recovery and an iron rich magnetic fraction suitable for recycling. Ideally, the most efficient separation of zinc will occur when the zinc is present as either ZnO or as a spinel of the type $Fe_{(1-x)} Zn_x Fe_2O_4$ for $0.7 < x < 1$. In this case, the zinc will remain in the non-magnetic fraction and the magnetic fraction will contain magnetite, Fe_3O_4, and maghemite, γ-Fe_2O_3.

The separation procedure involves ultrasonically dispersing the dust in proponol and extracting magnetic particles from the suspension using a weak magnet. The weight-fraction of magnetic material varied between 6% and 60% for different samples, averaging about 25%. Splits were characterized using SEM, x-ray diffraction and Mössbauer spectroscopy. The following results are shown for one sample taken to be representative of high zinc, low alloy carbon steel dust.

Several thousand individual particles were analyzed by the SEM automated image analysis technique. The results are shown in Table 3 for the bulk sample, the magnetic fraction and the non-magnetic fraction respectively. The data are presented in terms of the weight-percent of the most likely principle oxide type. Magnetic separation succeeds (at least partially) in concentrating much of the iron phase into the magnetic portion and likewise much of the zinc phase into the non-magnetic portion. Some residual zinc remains in the magnetic portion as mixed ferrite.

The x-ray diffraction data confirmed the presence of zinc oxide and zinc rich-zinc ferrite in the non-magnetic fraction along with some hematite; the magnetic fraction contains magnetite and some hematite as the major phases present with no trace of zinc oxide. The presence of hematite (a non-magnetic phase) in the magnetic fraction was found, upon further SEM examination, to be due to the precipitation of Fe_2O_3 within magnetic Fe_3O_4 particles (see Figure 11). Mössbauer studies confirmed the presence of a range of ferrite compositions thus accounting for the distribution of the ferrite between the magnetic and non-magnetic samples.

Non-magnetic specimens examined by STEM, contained large numbers of extremely small ZnO particles (often < 0.1 μm) and which had characteristic crystallographic habits, note Figure 12. Analysis of these particles showed that they can contain very small quantities of iron (approximately 1%) in

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[*] Many of these phases also contain varying amounts of substitutional elements such as Mn, Cr and Si.

[**] In this classification non-magnetic is taken to include weak paramagnetic behavior.

TABLE 2. CLASSIFICATION OF PRINCIPAL DUST PHASES ACCORDING TO THEIR MAGNETIC BEHAVIOR

Magnetic	Non Magnetic
Magnetite Fe_3O_4	Zinc oxide ZnO
Mixed ferrite $Fe_{(1-x)}\ Zn_x\ Fe_2O_4$; $0 < x < 0.7$	Mixed ferrite $Fe_{(1-x)}\ Zn_x\ Fe_2O_4$; $0.7 < x < 1$
Defect spinel γ-Fe_2O_3	Pure zinc ferrite $ZnFe_2O_4$
Elemental iron Fe	Hematite α - Fe_2O_3
	Minors CaO, SiO_2, etc.

TABLE 3. SEM ANALYSIS OF MAGNETICALLY SEPARATED ELECTRIC ARC FURNACE DUST

Oxide Type	% Bulk Sample	% Magnetic Fraction	% Non-Magnetic Fraction
Zinc Oxide	8	1	11
Iron Oxide	10	54	10
Mixed Ferrite	67	33	64
Calcium Oxide	4	1	7

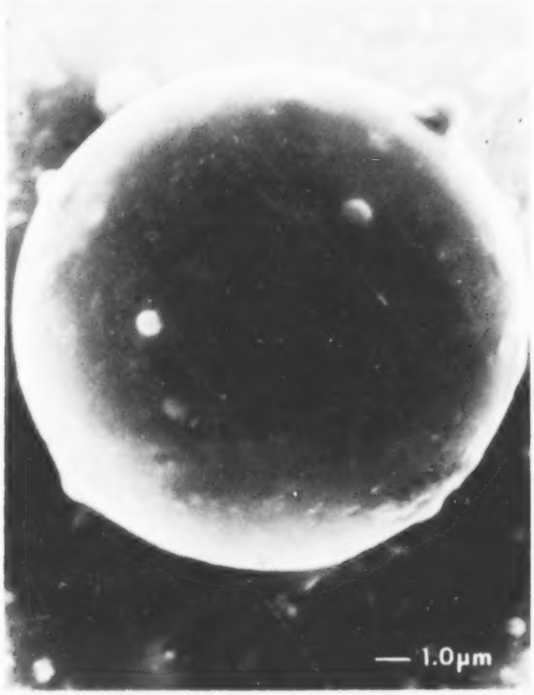

Figure 11: Large spinel particle containing dendritic hematite.

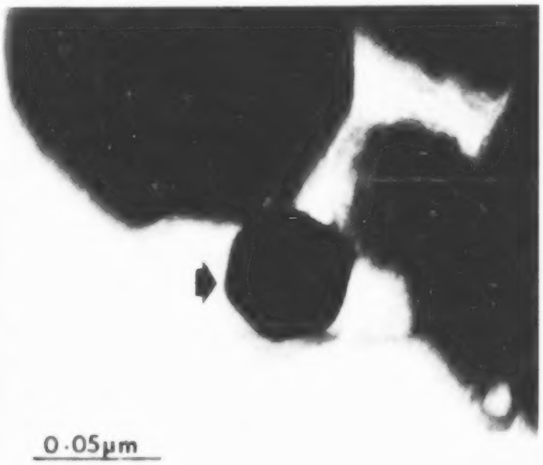

Figure 12: Zinc oxide particle, arrowed, in non-magnetic fraction.

solid solution. Chemical analysis of the non-magnetic fraction showed an increase in the total zinc content from 21.6 to 26.5 wt%.

It can be concluded that magnetic separation shows some promise as a process step in the recovery and recycling of electric furnace dust.

RECOVERY/RECYCLE OPTIONS

Most iron and steel plant iron and alloy bearing wastes are recycled through the sinter-plant blast-furnace complex. Steelmaking dusts from an electric-arc furnace are an exception because they contain undesirable impurities. Several interesting processes for recovering the inherent values have been under study.(2) In many cases the proposed economic practicability include credits by eliminating the high cost of disposal in commercial, regulated, or monitored landfills.

A schematic of the options for treating electric-arc furnace dust is shown in Figure 13. The following material summarizes some of the alternatives available today and some possible new options.

Changes in furnace operation may inhibit the formation of complex zinc containing spinels or the growth of particles which are not easily handled once they form in the fume. Such changes in procedures may facilitate separation techniques. Zinc and other volatile elements tend to be concentrated in the dust from the early part of the heat. Changing the method of fume collection could selectively remove a zinc concentrate. In addition magnetic separation as discussed earlier might further concentrate the zinc from the iron bearing dust. These options would require modification of the fume collection system.

There is a strong possibility that recycle processes such as injection or greenballing will concentrate the zinc,' lead, and cadmium to a sufficient degree (over 20%) to make them attractive for thermal recovery. Specific experiments are needed to substantiate this possibility.

Arc furnace dusts from stainless and specialty steelmaking are best treated by recycle techniques such as in-plant greenballing or briquetting with other alloy waste and recycling to the furnace,(3,4) or sending to a centralized processing plant.(5) The use of a better grade of scrap in the manufacture of these highly alloyed products provides much less potential for recovering the zinc, lead and cadmium.

Only in a few instances are the dusts, as produced, rich enough in the non-ferrous metals zinc, lead and cadmium to justify thermal recovery. It appears that in most dusts the recoverable elements need to be concentrated or purified before they can be shipped and treated in a recovery unit. There are limited opportunities for practical application of chemical solution treatments of arc furnace dusts from a technical, economical, and environmental standpoint. In carbon steel dusts, lead appears to be particularly troublesome. None of the leach treatments attempted in this study were effective in selectively removing lead to a safe level. Cadmium is relatively easy to remove to low levels. Of the chemical treatments available, only

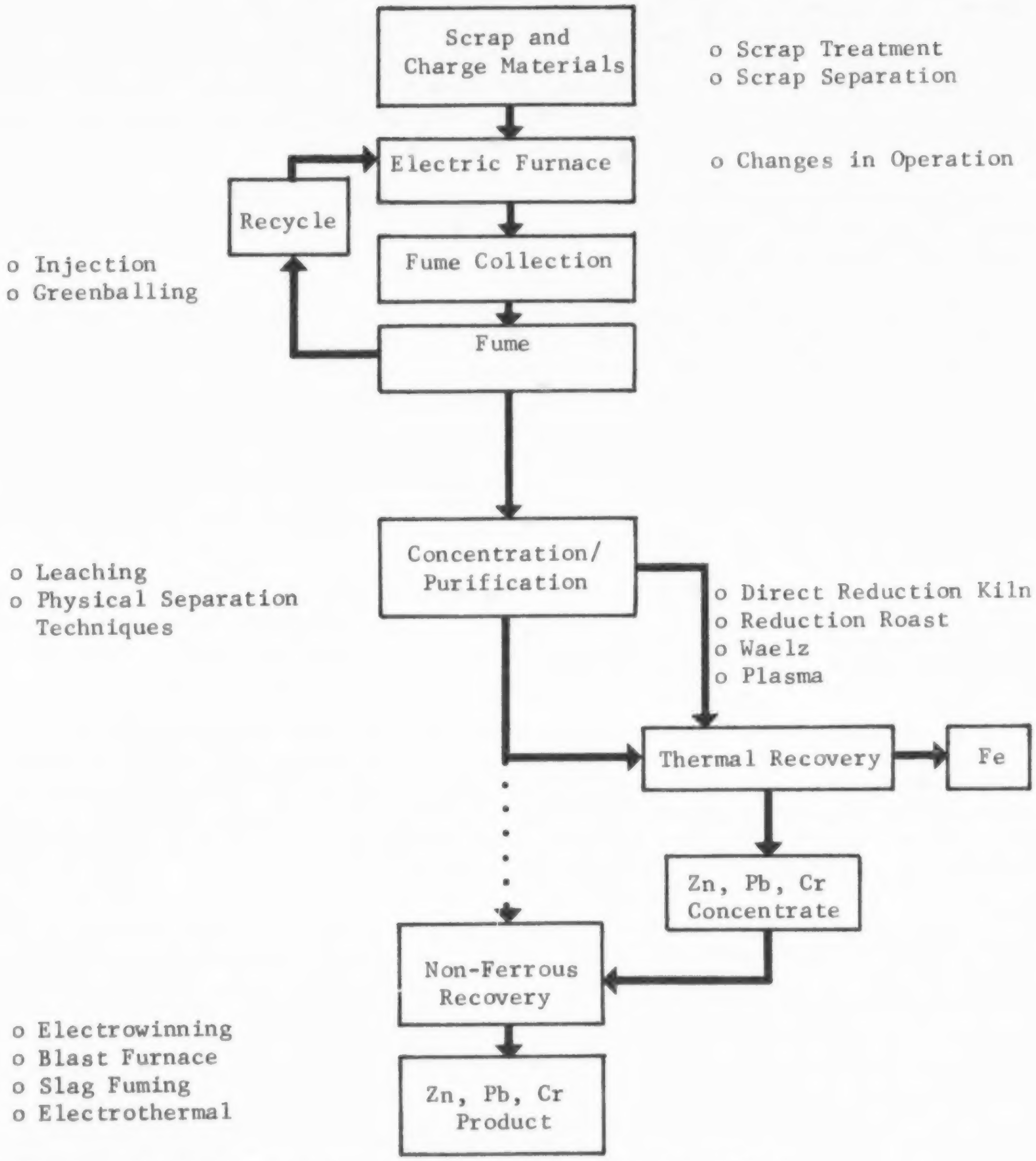
Scrap and Charge Materials
o Scrap Treatment
o Scrap Separation
Electric Furnace
o Changes in Operation
Recycle
Fume Collection
o Injection
o Greenballing
Fume
Concentration/ Purification
o Leaching
o Physical Separation Techniques
o Direct Reduction Kiln
o Reduction Roast
o Waelz
o Plasma
Thermal Recovery
Fe
Zn, Pb, Cr Concentrate
Non-Ferrous Recovery
o Electrowinning
o Blast Furnace
o Slag Fuming
o Electrothermal
Zn, Pb, Cr Product

Figure 13: Schematic for recycling and recovery options.

one or two appear to have any practical potential and none of these methods are ready for commercial applications. Various standard physical methods of separation were also attempted in this study on large quantities of furnace dust, but none of the techniques proved very successful. The concentration/purification option for furnace fume treatment still remains to be developed.

Chemical methods to extract zinc and lead from electric arc furnace dusts have emphasized the thermal recovery step. In most cases the tramp elements react with a suitable agent and transform volatile compounds which separate from the solid phases via the gas phase and are subsequently collected. The vaporization generally involves formation of volatile chlorides, volatile metal or oxides. Most of the processes that have progressed beyond the pilot stage consist of a direct reduction of the dust in a rotary kiln. These processes are carried out in the temperature range of between 950 and 1100°C. The gas flow rate is an important factor in carrying the vapors out of the bed into the gas stream where they are reoxidized. The product of these processes is an enriched oxide product. At lower temperatures the reduction and vaporization rates are too slow to be practical. At higher temperature physical-mechanical factors such as ringing in the kiln are limiting. In other processes, the temperature is raised to the range that the iron product and the gangue or slag are molten. This has the advantage of clean separation of slag from metal with the metal in a readily useable form. However the high temperatures require a large amount of energy.

Selective reduction and vaporization of zinc and lead in certain gaseous atmospheres which avoid reduction of iron oxides to metallic iron have been proposed. Depending on the composition of the dust over half the fuel requirement may be saved. A promising approach in today's technology is the reduction of iron in one zone of the kiln then reoxidizing it in another zone of the kiln in such a way that the heat of reduction is recovered in the process.

Serious efforts have been made by zinc smelters to recover zinc, lead and cadmium from steelmaking dusts. The contained zinc represents a significant potential domestic source of the metal. A German Company regularly operates a Waelz Kiln on electric arc furnace dust.(6) The Waelz Kiln is used to concentrate zinc, lead and cadmium from iron bearing zinc ores. The Waelz Kiln practice has been given a successful commercial trial in this country by the New Jersey Zinc Company. The product of the Waelz Kiln must be processed further to recover saleable products. A Japanese Company treats electric arc furnace dust in an electrothermic zinc furnace to produce a saleable zinc oxide product.(7) A new type of electrothermic furnace using plasma heat has been piloted in Sweden. Lead, zinc and iron were recovered in metallic form electric furnace dust. A pilot electrolytic zinc plant had promising results on high iron ores.(8) In the latter case, the dust was first given a reduction roast to break up the zinc ferrites.

The supply of zinc, lead, and cadmium in useable concentration from dust is variable. It would appear that the construction of new facilities to recover these non-ferrous elements may be justified if performed in conjunction with a direct reduction process to recover iron from a collection of iron bearing wastes. Unfortunately, impurities such as arsenic, antimony, germanium, nickel, iron, copper, cobalt and selenium reduce current efficiency and cause poor plating in electrolytic refining of zinc. Therefore removal of these elements further complicates the recovery of resources from electric arc furnace dust.

In summary there are a number of treatment options which can potentially concentrate iron and non-ferrous zinc, lead and chromium. It appears that zinc and magnetic concentration during fume collection and recycle options such as injection and greenballing are possible options that need further investigation.

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TREATMENT OF CARBON STEEL ELECTRIC FURNACE FLUE DUST BY SULFATION

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ABSTRACT

The zinc content of electric furnace flue dust can be sulfated by the action of iron sulfate in briquetted samples at 600-650°C. Up to 96% of the contained zinc is converted to water leachable zinc sulfate under optimum conditions. The other product is a relatively low zinc iron oxide. A Plackett-Burman statistical design was used to quantify the factors affecting the sulfation process. The mechanism of the process is explained by the use of thermochemical diagrams for the Fe-Zn-S-O system at different temperatures. The results suggest a process for rendering the electric furnace flue dust suitable for recycling into the steel plant flowsheet. The process may also be effective in detoxifying dust which does not otherwise pass the EP toxicity test.

INTRODUCTION

Large quantities of oxide dust are generated during the making of steel. The quantity of certain impurities in the dust, such as zinc, is dependent on the fraction of galvanized scrap used in the charge. In some cases, contents of zinc as high as 20% have been noted. The total zinc content of steelmaking furnace dusts has been calculated to equal 10% of the total mined zinc production in the U.S.[1]

Dust from iron and steelmaking operations has been normally dumped. Appropriate storage sites are becoming scarcer and more distant from the point of origin. Untreated dumps can lead to water pollution problems, especially if the dust is classified as a toxic substance. The zinc and iron values of these wastes remain unrecovered. This coupled with the high cost of dumping, has led industry to look at recycling for relief.[1,2,3]

The desirability of recovering iron units from the dust makes the blast furnace a logical point for recycling. However, zinc has been considered as the cause for many troubles in blast furnace operations, including refractory failure and scaffolding. More dramatic events like breakage of coolers, failure of the iron shell, complete filling of the gas offtakes and blocking of the bell can occur.[4,5] Zinc recovery from the dust therefore has two advantages. First, the zinc can be used to meet part of the requirements of industry and second, zinc removal may make the flue dust amenable, after agglomeration, to recycling into the blast furnace.

. Many methods have been proposed for flue dust recycling but only those involving zinc removal are mentioned here. There appears to be no dearth of published articles dealing with removal of zinc prior to recycling. Review articles[6,7] have described pyrometallurgical processes involving carbothermic reduction and chloridization; hydrometallurgical methods involving selective leaching with NH_4Cl, H_2O_2, H_2SO_4 or organic reagents and some less successful physical separation methods.

Heins[8] has developed a process whereby zinc rich flue dust can be used as an absorbent to reduce SO_2 emissions from industrial and public utility furnace flue gases, the zinc oxide and the ferrite being the most active absorbing agents. Umetsu and Suzuki[9] and Lenchev[10] have shown that a mixture of SO_2 and O_2 in the presence of a catalyst can effectively sulfate ZnO and $ZnFe_2O_4$ (zinc ferrite). Gaprindashvili *et al.*[11] have shown that ZnO and $ZnFe_2O_4$ can be almost completely sulfated when mixed with solid $FeSO_4$ at about 550°C.

In this paper a process is described for the removal of zinc from EFFD (electric furnace flue dust) which incorporates a steelmaking waste product derived from pickle liquor residue as the main ingredient. The process involves low temperature sulfation of the zinc by the action of either ferric or ferrous sulfate to produce soluble $ZnSO_4$ and a relatively low zinc-iron oxide residue. If need be, pickle liquor waste ($FeSO_4$) can be oxidized to $Fe_2(SO_4)_3$ prior to use, by a process described by Tiwari *et al.*[12] Two steel plant wastes, both difficult to dispose of, are thus converted into two potentially useful products.

THEORY OF SULFATION

The sulfation process involves a reaction between zinc compounds in the flue dust and the iron sulfates to produce $ZnSO_4$ and Fe_2O_3. In order for the above to occur, $ZnSO_4$ and Fe_2O_3 should be able to coexist in equilibrium. The Fe-Zn-S-O thermochemical system can show whether a co-stability region exists for the two compounds. The diagram can also help in determining equilibrium gas compositions. It has been shown that in the sulfation of zinc oxide and ferrite (the predominant zinc phases in flue dusts[8,13]), SO_3 is the sulfating species.[9,14] The composition of the sulfation gas is hence important in calculating the quantity of iron sulfate required to sulfate a given amount of zinc.

Thermochemical diagrams for the Fe-Zn-S-O system at 627°C (900 K) and 727°C (1000 K) are presented in Fig. 1. The data and reactions required for their construction are given in Table 1.

TABLE 1. THERMODYNAMIC DATA FOR SULFATION REACTIONS AT 900 AND 1000 K.

NO.	REACTION	TEMP T °K	log K_{rx}	ΔH°_{rx} at T(KJ)	DECOMPOSITION PRESSURE (ATM) WHERE APPROPRIATE	
1	$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$	900	-4.689	560.15	pSO_3 = 0.0274	
		1000	-1.465	558.85	pSO_3 = 0.325	
2	$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_2 + 1\frac{1}{2}O_2$	900	-7.164	854.22	pSO_2 = 0.0322	pO_2 = 0.0161
		1000	-2.236	851.7	pSO_2 = 0.401	pO_2 = 0.2005
3	$2FeSO_4 \rightarrow 0.321Fe_2(SO_4)_3 + 0.679Fe_2O_3 + SO_2 + 0.0369SO_3 + 0.00004O_2$	900	-0.1896	150.71	pSO_2 = 0.741	pO_2 = 0.00003
		1000	0.6747	108.06	pSO_3 = 0.0274	
					pSO_2 = 5.03 pSO_3 = 0.1856	pO_2 = 0.002
4	$2FeSO_4 + SO_2 + O_2 \rightarrow Fe_2(SO_4)_3$	900	4.646	-425.72		
		1000	1.928	-424.83		
5	$Fe_2O_3 + 2SO_2 + 3/2O_2 \rightarrow 2FeSO_4$	900	2.518	-428 5		
		1000	-0.463	-426.87		
6	$3Fe_2O_3 \rightarrow 2Fe_3O_4 + \frac{1}{2}O_2$	900	-6.28	252.76	pO_2 = $7x10^{-13}$	
		1000	-4.837	244.56	pO_2 = $2.1x10^{-13}$	
7	$3ZnSO_4 \rightarrow ZnO{\cdot}2ZnSO_4 + SO_3$	900	-3.168	224.82	pSO_3 = 0.00068	
		1000	-1.8627	224.82	pSO_3 = 0.0137	
8	$3ZnSO_4 \rightarrow ZnO{\cdot}2ZnSO_4 + SO_2 + \frac{1}{2}O_2$	900	-3.978	514.7	pSO_2 = 0.0028	pO_2 = 0.0014
		1000	-2.1197	517.67	pSO_2 = 0.0487	pO_2 = 0.02435
9	$3/2ZnFe_2O_4 + SO_2 + \frac{1}{2}O_2 \rightarrow \frac{1}{2}ZnO{\cdot}2ZnSO_4 + 3/2Fe_2O_3$	900	4.9796	321.24		
		1000	3.1919	361.83		
10	$3ZnO + Fe_2(SO_4)_3 \rightarrow 3ZnSO_4 + Fe_2O_3$	900	6.501	-122.9		
		1000	5.807	-114.18		
11	$3ZnO{\cdot}Fe_2O_3 + Fe_2(SO_4)_3 \rightarrow 3ZnSO_4 + 4Fe_2O_3$	900	5.94	-100.21		
		1000	5.402	- 84.49		
12	$ZnO + 2FeSO_4 \rightarrow ZnSO_4 + Fe_2O_3 + SO_2$	900	2.087	102.79		
		1000	2.64	104.91		
13	$ZnO{\cdot}Fe_2O_3 + 2FeSO_4 \rightarrow ZnSO_4 + 2Fe_2O_3 + SO_2$	900	1.9	110.36		
		1000	2 495	114.81		

The data for constructing the diagrams are from the following sources: ZnO, $ZnSO_4$ and $ZnO{\cdot}2ZnSO_4$ from an article by Kellogg and Ingraham,[15] $ZnFe_2O_4$ from Barin and Knacke[16] and iron compounds from JANAF.[17]

DECOMPOSITION OF IRON SULFATES

According to the thermochemical diagram, $Fe_2(SO_4)_3$ should decompose in inert atmospheres or vacuum, to Fe_2O_3, SO_2, SO_3 and O_2, the gas composition being labeled "a" in the diagram. The ratio of S:O in the gas is 1:3, which makes it completely useful in the sulfation of the zinc oxide phases. The decomposition temperature (temperature at which total decomposition gas pressure is one atmosphere) of $Fe_2(SO_4)_3$ was calculated to be 729°C (1002 K) by plotting the total decomposition pressure as a function of temperature.

$FeSO_4$ will initially decompose to $Fe_2(SO_4)_3$, to give an equilibrium gas

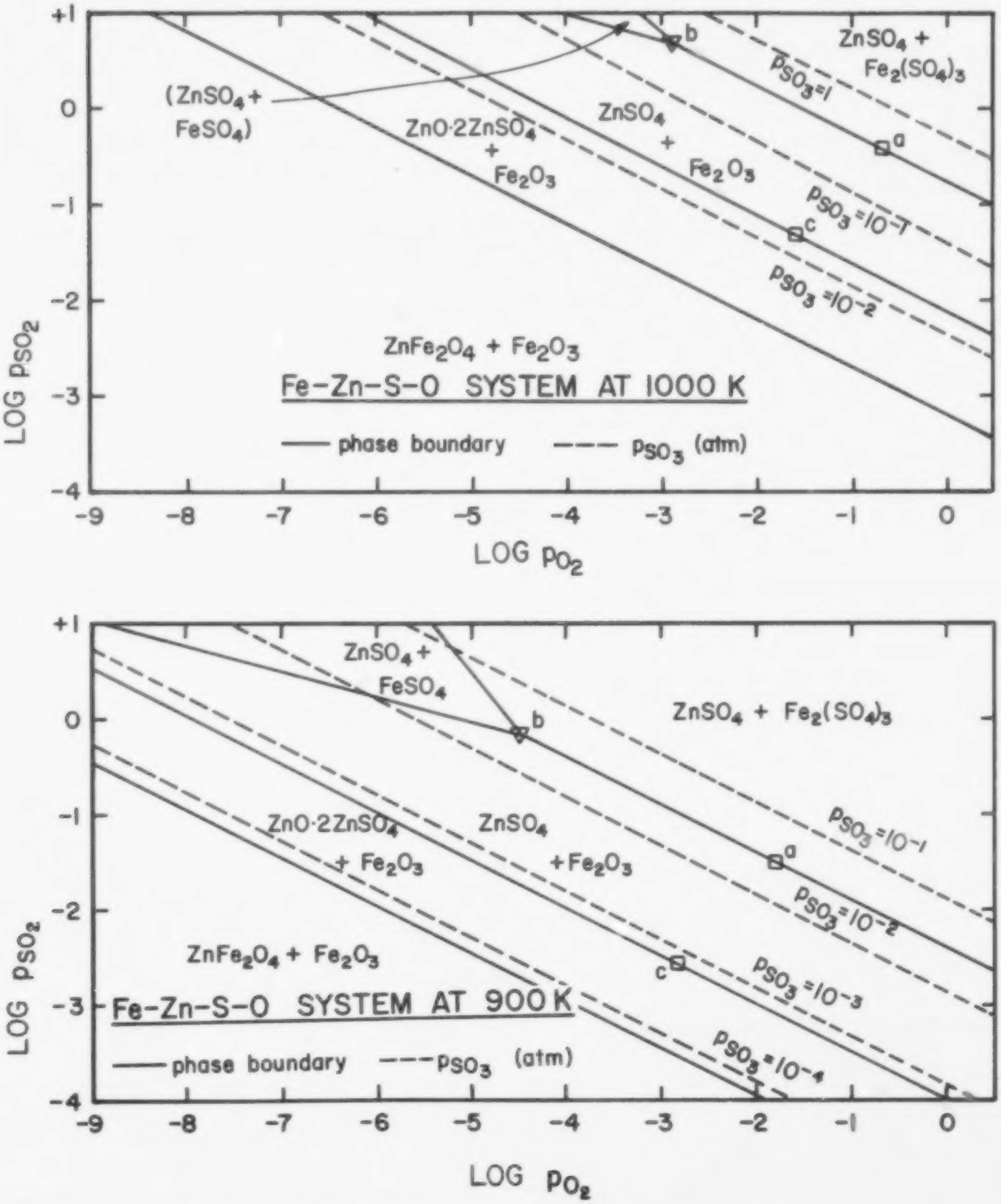

Figure 1. Thermochemical Diagrams for the Fe-Zn-S-O System at 900 and 1000 K.

composed mostly of SO_2, at the invariant point "b". SO_2 is of little use in sulfating zinc oxide compounds. The decomposition temperature was calculated to be 639°C (912 K). Once all the $FeSO_4$ has decomposed, the $Fe_2(SO_4)_3$ formed will decompose in the manner indicated previously. The secondary decomposition gases in the above case arise from the decomposition of $Fe_2(SO_4)_3$ and are therefore completely useful in the sulfation process.

SULFATION OF ZnO

In order to sulfate ZnO, the reaction gases must contain SO_2, O_2 and SO_3 at pressures in excess of that required for the thermal decomposition of $ZnSO_4$. The first step in $ZnSO_4$ decomposition is the formation of basic sulfate[15] which is indicated by point "c" on the thermochemical diagrams (Fig. 1) The decomposition temperature for $ZnSO_4$ was calculated to be 853°C (1126 K). The diagram shows that at 627°C (900 K) the decomposition pressure for $ZnSO_4$ is over an order of magnitude less than the decomposition pressure for either of the iron sulfates. Equations 7 and 8 of Table 1 show that the decomposition gases of $ZnSO_4$ have an S:O ratio of 1:3, which means that the most effective sulfating gas must also have the same S:O ratio.

From the previous discussion it would follow that when the system has zero gas volume, one mole of $Fe_2(SO_4)_3$ will sulfate three mols of $ZnO/ZnFe_2O_4$. On the other hand two mols of $FeSO_4$ will first decompose to produce 0.037 mols of SO_3 gas capable of sulfating 0.037 mols of $ZnSO_4$. Subsequent decomposition of 0.321 mols of $Fe_2(SO_4)_3$ will sulfate 0.963 mols of $ZnO/ZnFe_2O_4$. Therefore, two mols of $FeSO_4$ are capable of sulfating only 1 mole of $ZnO/ZnFe_2O_4$. The major sulfating action of $FeSO_4$ thus comes from the secondary $Fe_2(SO_4)_3$ decomposition.

The thermochemical diagrams indicate a moderately sized region of co-stability for $ZnSO_4$ and Fe_2O_3 at oxygen pressures greater than 10^{-5} atm. At 727°C (1000 K) and oxygen pressures of 0.21 atm. such as those found when operating in air, the SO_2 pressures required for $ZnSO_4$ stability are about 0.01 atmosphere or more. The SO_2 pressure is an order of magnitude lower at 627°C (900 K) than at 727°C (1000 K) for $ZnSO_4$ stability and hence easier to maintain. $ZnSO_4$ stability increases at lower temperatures; the equilibrium SO_3 pressures for the iron sulfates decrease and therefore the amount of sulfating species (SO_3) present in the gases is also lower. Thus a competition exists between more favorable thermodynamics at lower temperatures, and higher reaction rates and SO_3 content at higher temperatures. The result is an optimum sulfation temperature which must be determined by experiment. Therefore, one of the objectives of this work was to determine the effect of temperature on zinc sulfation (and recovery). However, other variables will also affect zinc sulfation; temperature cannot be considered independent of these. This situation requires care in experimental design, as will be discussed.

The presence of carbon or CO gas in the system would reduce the oxygen partial pressure, meaning that a higher SO_2 partial pressure must be developed to keep the system in the Fe_2O_3 + $ZnSO_4$ region. Thus the presence of carbon is detrimental to the sulfation reaction and also aids in $ZnSO_4$ decomposition.[18]

The sulfation of $ZnFe_2O_4$ and ZnO is shown as equations 10 and 11 in Table 1. ΔH°_{rx} for both reactions is negative; therefore energy has to be supplied only to heat the reactants to the reaction temperature and not for the reaction itself. If $FeSO_4$ is used, the primary decomposition to $Fe_2(SO_4)_3$ is very endothermic (ΔH°_{rx} = +452.14kJ) as per reaction 3 of Table 1 at 627°C (900 K). The overall sulfation reaction (primary and secondary decomposition of $FeSO_4$ and sulfation of-zinc compounds) is exothermic.

The discussion has shown that when conditions at 627°C (900 K) are compared to those at 727°C (1000 K), the lower temperature results in lower SO_3 pressures for co-stability of Fe_2O_3 and $ZnSO_4$. When $Fe_2(SO_4)_3$ is used as a sulfating agent, the best system is one in which the gas volume approaches zero. A pellet made up of a mixture of flue dust and the sulfate is the closest practical approximation to this condition.

If $FeSO_4$ is used, a good way to carry out the sulfation might be to heat the mixture in a loose bed in air so that oxygen is available. Oxygen assists the sulfation by reacting with SO_2 to form the sulfating species SO_3. The use of a loose bed, however, results in some loss of SO_2 to the surroundings..Experiments are thus necessary to determine if a pellet or a loose bed is better for sulfation using $FeSO_4$.

The discussion to this point indicates that $Fe_2(SO_4)_3$ has certain theoretical advantages over $FeSO_4$ as a sulfating agent. The source of $Fe_2(SO_4)_3$ should make no difference. It can be added as the solid sulfate, or be formed in situ by adding sulfuric acid to the dust.

OTHER SULFATION REACTIONS

Many metal oxides other than zinc are expected to be sulfated by iron sulfate. Thermodynamic calculations similar to the foregoing indicate that the oxides of the following metals should be sulfated by iron sulfate: Cu, Pb, Cd, Mn, Mg, Ca, K, Na, and Ni. Thus a calculation of the sulfation "demand" by the dust involves the sulfation of these elements, as well as the zinc.

EXPERIMENTATION

An industrially generated electric furnace flue dust (EFFD) sample was used in this study. Ferrous sulfate in the form $FeSO_4 \cdot 7H_2O$, obtained from a pickle liquor plant reclamation process, and ferric sulfate as laboratory grade $Fe_2(SO_4)_3 \cdot xH_2O$ were used as sulfating reagents.

SAMPLE CHARACTERIZATION

Characterization involved x-ray, surface area, DTA and TGA studies. Leaching tests were used to determine the concentration of the zinc phases in the EFFD. The gases from thermal decomposition of iron sulfates were analyzed by an absorption method.

To determine the total zinc content, the sample was digested in 30% H_3PO_4 solution and the resulting solution was analyzed for zinc on a Perkin-

Elmer atomic absorption unit. The zinc as ZnO was determined by first leaching the EFFD in dilute H_2SO_4 (pH = 1.1), after which the solution was filtered and the filtrate analyzed by AA.

DTA and TGA graphs were obtained up to 950°C in air and nitrogen on the EFFD sample, $ZnSO_4$, and the two iron sulfates, using a Mettler apparatus. The phases produced during decomposition of the iron sulfates after heating to various temperatures for about half an hour were determined by x-ray analysis of the products.

The sulfur content of EFFD was determined with a Leco analyzer. Other elements were analyzed by the supplier of the dust sample.

EXPERIMENTAL STRATEGY

The factors affecting the sulfation process were studied with the help of a Plackett-Burman screening design. The P-B screening design is a statistical experimental design which aids in an organized approach towards the collection and analysis of information.[19]

The values of the independent variables (factors) are set so that the entire experimental region of interest is investigated. A large number of experimental values is obtained by performing tests throughout the experimental region, i.e., at high, low, and mean levels for each independent variable. The P-B design permits a relatively large amount of information to be gathered from a limited number of experiments since all variables are changed simultaneously.

The data obtained from the tests are used to calculate the main effect estimate which represents the change in response to the levels. The precision of each main effect estimate is generally stated in the form of a confidence interval, calculated at a fixed confidence level. A level of 90% is most commonly accepted for industrial experiments and was the value used in this study. An effect is said to be significant if the confidence interval does not include zero. Only the significant effects are used in calculating an expression for the response in terms of the factors studied.

In this study an eight run screening design was used.[19] A total of five factors was studied, which allowed for two dummy variables (to detect interaction). Three center point experiments were carried out. Each of the eight design runs was duplicated to give an idea of the reproducibility of the measured response in percent zinc recovery. This made a total of nineteen experimental runs.

EXPERIMENTAL PROCEDURE

The influence of certain variables thought to affect the sulfation process was evaluated in a number of preliminary laboratory tests. Results of these tests were used to select the P-B screening test conditions as shown in Table 2.

TABLE 2. INDEPENDENT VARIABLES AND THEIR RANGES

	Low	High	Center Point
Temperature	600°C	650°C	625°C
Time	30 min	50 min	40 min
Stoichiometry (mols of iron sulfate per mol of zinc)	2:1	3:1	2.5:1
Pellet diameter	1.27 cm	2.54 cm	1.91 cm
Type of sulfate	$FeSO_4$	$Fe_2(SO_4)_3$	50:50*

*50:50 indicates that half the "SO_4" added is contributed by $FeSO_4$ and the other half by $Fe_2(SO_4)_3$.

Iron sulfates were dried in air at 300°C before use. The dehydrated sulfates and the EFFD were crushed and the -65 mesh fraction was used in this study. Required amounts of EFFD and the appropriate sulfate were weighed out and mixed with a mortar and pestle. Enough mixture to form a 2.54 cm high pellet, after pressing, was weighed and pressed at 155 MPa (22,500 psi) in a Carver laboratory press. The pellets were then reacted in a tube furnace under the required conditions. The time allowed for the reactions was measured from the instant the pellet was introduced into the furnace. A thermocouple was introduced into the center of a dummy pellet (1.27 cm diameter) and the pellet at room temperature was introduced into the furnace. Four minutes were required for the center of the sample to reach within 10° of the furnace temperature (650°C). An air flow of 47.2 cm^3/sec was maintained through the furnace during the sulfation.

On the completion of the run, the sample was immediately air-cooled. The cooled sample was weighed, crushed to -65 mesh, and leached overnight in distilled water. The solution was then filtered and the residue washed and dried in air. The leach solution was diluted to give an expected zinc concentration in the range of 2-4 ppm and analyzed for zinc by AA. The sulfur content of leach residues was also determined.

The study of zinc sulfation as a function of time was performed under the following conditions: temperature, 650°C; stoichiometry, 3:1; sulfate, $Fe_2(SO_4)_3$; and size, 1.27 cm diameter. Duplicate samples were prepared, sulfated and analyzed in the same manner mentioned earlier. Zinc recoveries were measured after 5, 10, 20, 25, 30 and 45 minutes at 650°C.

EP TOXICITY TESTS ON AS-RECEIVED AND SULFATED DUST

Various carbon-steel EF dusts have been reported as exceeding allowable limits of soluble lead and cadmium when tested according to published EP toxicity test procedures. However, in theory, the sulfated and water-leached dusts should give much lower results for lead and cadmium than the as received dusts for two reasons: cadmium sulfate is water-soluble and should tend to follow the zinc, which is extensively removed; and lead sulfate is relatively insoluble and should not be leached. In order to test these hypotheses, EP toxicity tests were run on two different EF dust samples. For purposes of comparison, both dusts were tested for toxicity in the as-received condition, and after sulfation and water leaching. The dusts were obtained from two different steel producers, and both contained over 14% zinc.

Toxicity tests of the as-received and sulfated/water leached dust were performed on 100 g samples, according to the EP toxicity test procedure listed in Appendix II of the Federal Register, vol. 45, #98, May 19, 1980, p 33127. In summary, the EP test procedure involves adding water and acetic acid to the solid waste until the pH reaches 5, and agitating for 24 hours. The mixture is filtered through an 0.45 micron filter, and the filtrate analyzed by AA. If the solid waste has a pH of 5 or less after adding water, no acetic acid is added.

Sulfation conditions were selected to provide maximum recovery of zinc as $ZnSO_4$, and were as follows: 600°C, 30 min, 1.91 cm pellet diameter, and 3 mols of SO_4 added (as $Fe_2(SO_4)_3$). Following the sulfation process, the pellets were crushed to -35 mesh, and leached in water overnight. The filtrate was analyzed for Zn, so as to determine the %Zn recovery. The filter cake was dried at 150°C, and crushed to -35 mesh (actually, the filter cake practically falls apart in the mortar and pestle to a rather fine powder and a few small lumps). The filter cake is then subjected to the EP toxicity test.

RESULTS AND DISCUSSION

CHARACTERIZATION OF THE EFFD

The chemical and x-ray analysis of the EFFD sample are presented in Table 3. The major phases indicated are shown in Part B of the table.

TABLE 3. CHARACTERIZATION OF EF DUST

A) CHEMICAL ANALYSIS

Total Fe	CaO	MgO	Al_2O_3	SiO_2	Mn	Cr	Na_2O
32.8%	3.3%	3.8%	0.6%	2.3%	4.8%	0.1%	0.7%
	K_2O	S	P	Zn	Pb	C	
	1.2%	0.3%	0.18%	16.4%	1.6%	0.3%	

B) X-RAY ANALYSIS

Major phases: ZnO, Fe_2O_3, Fe_3O_4, possibly $ZnFe_2O_4$

C) ACID LEACHING TEST

Total Zinc	16.4%
Zn leached out in H_2SO_4	14.2
% Zn as ZnO	86.6

D) SURFACE AREA

As-received EFFD	<0.26 m^2/g
Dried at 125°C, 1 hr, air	2.94 m^2/g

The presence of $ZnFe_2O_4$ is difficult to detect with x-rays since the pattern coincides with that of Fe_3O_4. Dilute H_2SO_4 leaching tests indicate that about 85% of the zinc is as ZnO. The rest of the zinc is probably present as the ferrite. This is in agreement with the findings of Heins[8] and Fosnacht.[13]

Surface area measurements on as received EFFD show a specific surface area of less than 0.26 m^2/gm. A larger surface area (2.94 m^2/g) was obtained after the sample was heated. This indicates the presence of capillary type porosity (which is sealed up when moisture is present).

THERMAL ANALYSIS AND DECOMPOSITION STUDIES

The DTA and TGA curves of EFFD showed that the flue dust was relatively inert to air roasting. The absence of any appreciable weight loss indicated that the C or other organics which could reduce the stability of $ZnSO_4$ are not present.

Three distinct regions are observed on the DTA curves of iron and zinc sulfate, as presented in Fig. 2.

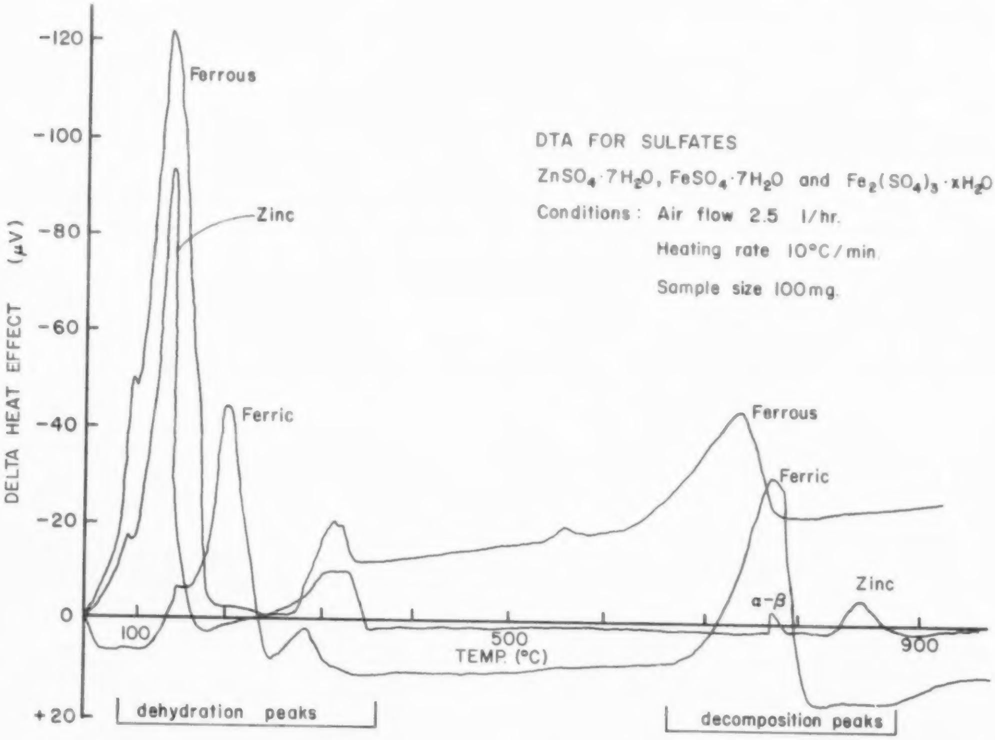

Figure 2. Differential thermal analysis in air for iron sulfates and zinc sulfate.

First, from 100 to 300°C, the water of hydration is evolved, the last water molecule being driven off around 300°C. In the second region $ZnSO_4$ and $Fe_2(SO_4)_3$ shown no changes, whereas $FeSO_4$ gives a small exothermic peak around 500°C. In the third region all the sulfates decompose. The iron sulfates decompose to Fe_2O_3 at a maximum rate near 700°C, although the effects are seen to initiate at about 600°C. The $ZnSO_4$ shows an α-β transformation at 750°C and a decomposition to $ZnO \cdot 2ZnSO_4$ around 800°C. The DTA curves show that $FeSO_4$ decomposition depends on the gas medium used, but $Fe_2(SO_4)_3$ or $ZnSO_4$ do not. The DTA curves indicate that the region of interest for sulfation is between 600° and 750°C, where the iron sulfates decompose readily but $ZnSO_4$ is relatively stable. The preliminary tests to set design limits for P-B screening were conducted in this range.

The cooled reaction products produced by decomposing the iron sulfates at various temperatures were identified by x-rays. The phases detected helped determine the decomposition sequence of the iron sulfates which is given in Table 4.

TABLE 4. DECOMPOSITION SEQUENCE FOR IRON SULFATES

		REACTION	TEMPERATURE
1) $FeSO_4 \cdot 7H_2O$ - AIR:			
$FeSO_4 \cdot 7H_2O$	→	$FeSO_4 \cdot H_2O$	150°C
$FeSO_4 \cdot H_2$	→	$FeSO_4$	300°C
$4FeSO_4 + 1/2O_2$	→	$Fe_2(SO_4)_3 + Fe_2O_3 + SO_2$*	550°C
$Fe_2(SO_4)_3$	→	$Fe_2O_3 + 3SO_2$** $+ 3/2O_2$	600°C
NITROGEN:			
$FeSO_4 \cdot 7H_2O$	→	$FeSO_4 \cdot H_2O$	150°C
$FeSO_4 \cdot H_2O$	→	$FeSO_4$	300°C
$2FeSO_4$	→	$Fe_2O_2SO_4$*** $+ SO_2$	300-500°C
$3Fe_2O_2SO_4$	→	$Fe_2(SO_4)_3 + 2Fe_2O_3$	550°C
$Fe_2(SO_4)_3$	→	$Fe_2O_3 + 3SO_2$** $+ 3/2O_2$	600°C
2) $Fe_2(SO_4)_3 \cdot xH_2O$:			
$Fe_2(SO_4)_3 \cdot xH_2O$	→	$Fe_2(SO_4)_3 \cdot H_2O$	150°C
$Fe_2(SO_4)_3 \cdot H_2O$	→	$Fe_2(SO_4)_3$	300°C
$Fe_2(SO_4)_3$	→	$Fe_2O_3 + 3SO_2$** $+ 3/2O_2$	600°C

*Some SO_3 is present but in very small amounts.

**Moderate amounts of SO_3 are also expected to be present.

***This is a nonequilibrium compound and was identified by Gallagher et al.[21] The x-ray data to determine this phase were obtained from Skeaff and Espelund.[20]

The DTA curves indicate that the thermal decomposition peak for $Fe_2(SO_4)_3$ produced from $FeSO_4$ occurs at slightly lower temperatures than the reagent grade $Fe_2(SO_4)_3$. This is expected due to the more reactive nature and smaller particle size of nascent $Fe_2(SO_4)_3$, as compared to laboratory grade $Fe_2(SO_4)_3$.

SO_2 EMISSIONS DURING DECOMPOSITION

The results from SO_2 emission measurements are presented in Fig. 3 and 4. Fig. 3 shows iron sulfate and EFFD/$Fe_2(SO_4)_3$ mixture decomposition curves in air, and Fig. 4 represents iron sulfate decomposition in Ar. The air decomposition curves for iron sulfates with and without EFFD are comparable, which indicates that the presence of EFFD does not appreciably change the SO_2 emissions from the sulfates.

The iron sulfate decomposition curves in air show a sharp decrease in SO_2 before leveling off. This drop is probably caused by conversion of SO_2 to SO_3 by air oxidation. Freshly formed Fe_2O_3 is known to be a catalyst for SO_3 formation[22] and hence results in a lowering of the SO_2 pressure. This is confirmed by similar curves in Ar, which show a higher SO_2 content and no sharp decline prior to leveling off.

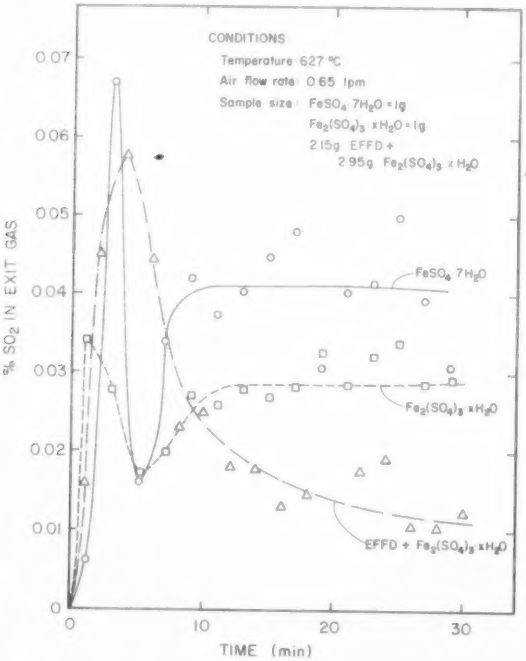

Figure 3. Air decomposition curves for iron sulfates and mixture of EFFD and $Fe_2(SO_4)_3 \cdot x\,H_2O$

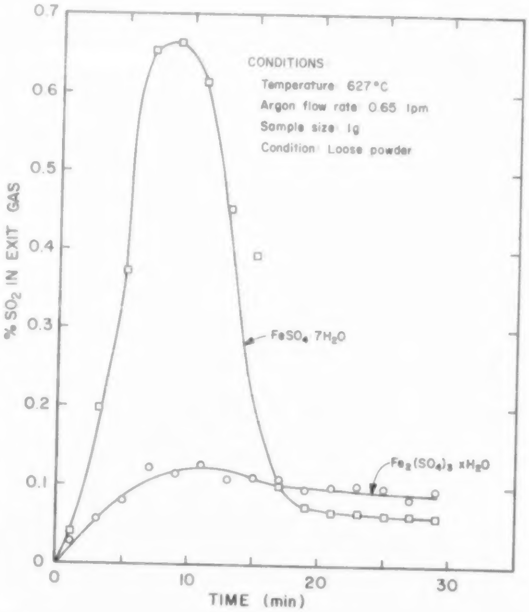

Figure 4. Argon decomposition curves for iron sulfate.

The effect of lack of O_2 is more pronounced in the case of $FeSO_4$. In Ar, $FeSO_4$ gives off much larger amounts of SO_2 during decomposition than in air; the difference in the case of $Fe_2(SO_4)_3$ is minimal. This shows that in the presence of air the SO_2 was substantially oxidized to SO_3 thus increasing the sulfation potential of $FeSO_4$. If all the SO_2 produced can be oxidized then the amount of zinc that sulfates could be doubled.

PLACKETT-BURMAN SCREENING TESTS AND RESULTS

The P-B screening test design is presented in Table 5. Table 6 contains the results and calculations corresponding to the P-B tests.

TABLE 5. COMPLETE DESIGN WITH CENTER POINTS OF THE RUN

RUN NO. AFTER RANDOM ORDERING AND INCLUDING CENTER POINTS	x_1 TEMP. (° C)	x_2 TIME (MINS)	x_3 TYPE OF SULFATE	x_4 STOICH. OF SULFATE ADDED	x_5 SIZE (INCHES)	x_6 (DUMMY)	x_7	ORIGINAL RUN NO.
I	625	40	50:50	2.5:1	3/8			Center Point
II	- 600	+ 5[illegible]	- $FeSO_4$	+ 3:1	- 1/4	+	-	3
III	+ 650	- 30	+ $Fe_2(SO_4)_3$	- 2:1	- 1/4	+	-	6
IV	+ 650	- 50	- $FeSO_4$	- 2:1	- 1/4	-	+	4
V	- 600	+ 50	+ $Fe_2(SO_4)_3$	- 2:1	- 1/2	-	-	7
VI	625	40	50:50	2.5:1	3/8			Center Point
VII	- 600	- 30	+ $Fe_2(SO_4)_3$	+ 3:1	- 1/4	-	+	5
VIII	+ 650	- 30	- $FeSO_4$	+ 3:1	+ 1/2	-	-	2
IX	+ 650	+ 50	+ $Fe_2(SO_4)_3$	+ 3:1	+ 1/2	+	+	8
X	- 600	- 30	- $FeSO_4$	- 2:1	+ 1/2	+	+	1
XI	625	40	50:50	2.5:1	3/8			Center Point

'+' refers to the high level of the factors, and '-' the low level.

The confidence limit interval results show that at the 90% level, all factors are significant. The dummy variable x_7 is also significant, which means that interaction between variables (like x_1x_2, or x_3x_4) is a significant possibility. More extensive experimental work is needed to construct a second order model that takes into consideration the various interaction possibilities.[19]

Standard statistical model-fitting procedures were used to construct an equation relating zinc recovery to the experimental variables. The variables used in the equation are listed on Table 7, and the resulting equation presented at the bottom of the table. The value of S in the table and the model represents the fraction of sulfur in the mixture of sulfates that is provided by $Fe_2(SO_4)_3$. Although the % Zn recovered is probably significant only to two significant figures, more figures are retained in the equation to improve internal consistency.

TABLE 6. P-B SCREENING TEST RESULTS

A) ZINC RECOVERIES

Run No.	I	II	III	IV	V	VI	VII
Zn Recovery, %	74.4	88.5	81.5	58.8	86.7	73.8	94.7

Run No.	VIII	IX	X	XI
Zn Recovery, %	96.6	93.4	71.9	75.0

B) CONFIDENCE INTERVAL CALCULATION

VARIABLE	MAIN EFFECT ESTIMATE	CONFIDENCE INTERVAL AT 90%
x_1(temperature)	-2.88	-1.89 to -3.88
x_2(time)	-4.33	-3.34 to -5.33
x_3(type of sulfate)	10.11	11.11 to 9.12
x_4(stoichiometry)	18.56	19.56 to 17.57
x_5(size)	6.28	7.28 to 5.29
x_6(dummy)	-0.36	0.6325 to -1.3575
x_7(dummy)	-8.13	-7.1425 to -9.1325

TABLE 7. VARIABLES USED IN FIRST ORDER MODEL

VARIABLE	NO. IN DESIGN	SYMBOL USED IN MODEL	UNITS
Temperature	x_1	T	°C
Time	x_2	t	min
Sulfate	x_3	S	0 = $FeSO_4$ 1 = $Fe_2(SO_4)_3$
Stoichiometry	x_4	X	
Size	x_5	r	pellet radius, cm

Zn Recovery, % = $67.9 - 0.0578T - 0.217t + 10.1S + 18.56X + 9.91r$

The model predicts that maximum zinc recovery is obtained by operating at lower temperatures, shorter times, larger diameter pellets, and use of larger amounts of ferric sulfate. To test the accuracy of the model, the calculated and experimental results were plotted as shown in Figure 5. The center points give an idea of the amount of curvature, or deviation, from a linear model. The linear model seems to fit the system well, since the center point results are about 10% off, and the other points no more than 6% off.

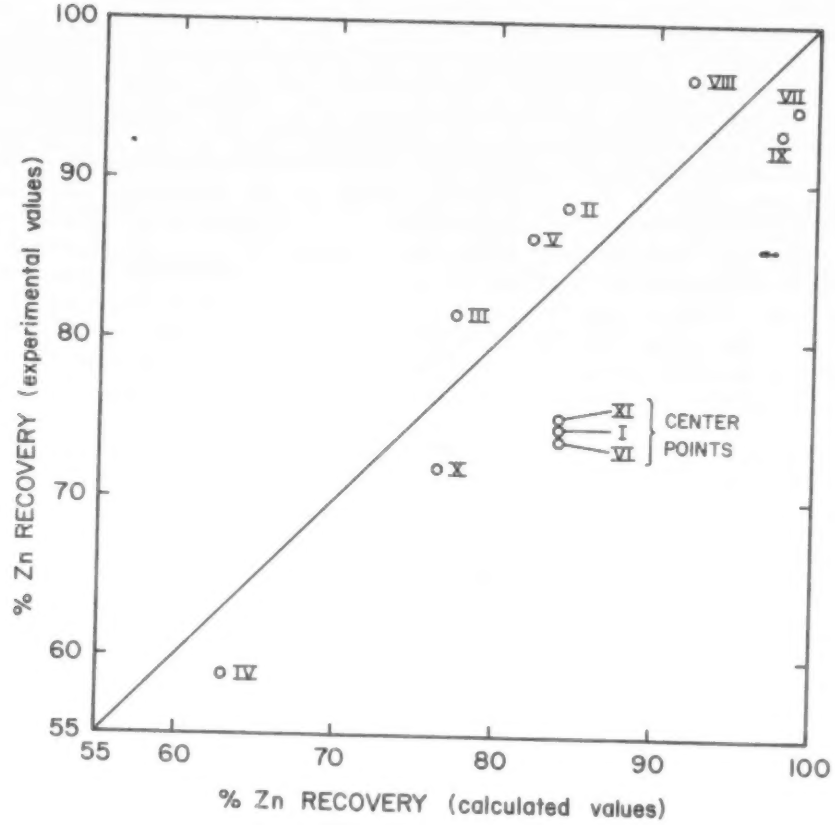

Figure 5. Experimental values versus calculated values from linear model.

The results generally conform to what would be expected from thermodynamic and kinetic considerations. The stoichiometry of ferric sulfate favors it as a sulfating agent over ferrous sulfate. The difference in decomposition pressures between ferric sulfate and zinc sulfate is greater at lower temperatures. Also, the shorter times and larger pellets tend to minimize thermal decomposition of zinc sulfate. Thus, the results of a series of statistically-designed zinc sulfation and leaching tests on a typical EF dust were shown to be amenable to a mathematical anaylsis which showed good agreement with a linear model.

The sulfur content of the leached residues averaged 2.5%, and varied from 1.6 to 4.2%. The sulfur level was affected most by the type of sulfate, amount of sulfate and size of the pellet. The effect of temperature was somewhat less significant. Further studies are required to minimize sulfur levels in leach residue and to identify the sulfur-containing phases.

TEST OF ZINC RECOVERY MODEL ON ANOTHER SAMPLE OF EF DUST

The model developed above was based entirely on experiments with the dust described in Table 3. In order to test the general applicability of the model, sulfation and zinc recovery tests were made on a second sample from the same company. The two dust samples differed mainly in their zinc and calcium composition (first dust: 3.3% CaO, 16.4% Zn; second dust: 9.6% CaO, 14.7% Zn), although most other elements showed some significant differences as well. Pellets of both dusts were prepared according to the center point conditions listed in Table 2 and sulfated together in the furnace. The results of the tests are shown in Table 8. In addition, a larger scale center point sulfation test was conducted by placing 24 pellets in a combustion tube, and slowly moving the tube through the hot zone of the furnace. The experiment was performed twice. The resultant pellets were divided into four equal portions and leached in a stagewise manner, so as to obtain a more concentrated solution for zinc electrowinning tests. The results are shown in Table 9.

TABLE 8. CENTER POINT SULFATION TESTS OF TWO EF DUST SAMPLES

	Dust #1				Dust #2			
Sample No.	1	2	3	4	1	2	3	4
Zn Recovery, %	81.8	84.4	86.2	85.6	83.2	85.4	84.3	86.5

TABLE 9. LARGE SCALE CENTER POINT LEACHING TEST RESULTS WITH DUST #2 FOUR-STAGE COUNTER CURRENT LEACHING PROCEDURE

Batch No.	1	2	3	4
Zn Recovery, %	78.7	78.3	66.0	50.0

According to the model equation given at the bottom of Table 7, 84% zinc recovery should have been obtained from all tests. The results in Table 8, using the standard leach procedure, show that two different dusts, with significant composition differences, behave about the same and are in good agreement with the model. The results in Table 9 show that fairly good agreement with the model is attained in the first two leach stages, but extraction in subsequent stages with the same leach solution give successively poorer results. This is probably caused by the buildup of zinc in the filtrate, which left an increasing amount of zinc in the filter cake (which was about 70% solids).

Another larger-scale test was made on dust #2, for the following sulfating conditions: 600°C for 30 min, 3:1 stoichiometry with ferric sulfate and 1.91 cm diameter pellets. 95% of the zinc was recovered, as compared to 102% predicted from the model equation. The agreement with experimental and predicted results is again within about 5%, as was found at other conditions.

EP TOXICITY TESTS

The results of the EP toxicity test are expressed as ppm in the filtrate. The filtrate was analyzed by AA, according to two methods: method of standard addition (SA), and calibration curve method (CC). The results were usually not the same. Both results are presented in the table below. Note that the EP toxicity test does not specify a toxic limit for zinc, but we have analyzed the filtrate for zinc anyway, and reported the results in the table.

TABLE 10. EP TOXICITY TEST RESULTS ON AS-RECEIVED AND SULFATED EF DUST SAMPLES

Sample	Zn		Pb		Cd	
	SA	CC	SA	CC	SA	CC
Ohio plant, as-rec'd.	2800	2500	84.3	87.9	6.8	6.5
Ohio plant, sulfated*	15	14	3.8	3.6	0.16	0.16
Illinois plant, as-rec'd.	1590	1340	103	104	11.6	11.8
Illinois plant, sulfated**	36	29	3.7	3.9	3.5	3.7

*91% Zn recovery
**95% Zn recovery

The results of the as-received vs. sulfated dust samples show that the sulfation procedure tends to fix lead as the relatively insoluble $PbSO_4$, while cadmium is generally sulfated to the relatively soluble $CdSO_4$, and tends to follow zinc in that regard.

CONCLUSIONS

Zinc compounds in electric furnace flue dust can be readily sulfated by iron sulfates in the temperature range 600° to 650°C. Almost 95% of the contained zinc can be converted into water leachable $ZnSO_4$. A statistical analysis of the results show that temperature, time of reaction, size of pellet and amount and type of sulfate are all important in affecting the sulfation process. After agglomeration, the low-zinc residues may be recycled to the blast furnace. If recycling is not feasible, the residue may be landfilled under a less toxic classification than in the original condition.

ACKNOWLEDGEMENTS

The authors are grateful to Inland Steel Corporation for providing chemical analyses, and to the National Steel Corporation for a Fellowship and financial assistance. We also wish to acknowledge financial assistance provided by a State Mining Institute grant allotment.

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PANEL: DESTRUCTION OF HAZARDOUS WASTE IN IRON AND STEEL FURNACES

ENGINEERING REQUIREMENTS FOR THERMAL DESTRUCTION OF HAZARDOUS WASTE IN HIGH TEMPERATURE INDUSTRIAL PROCESSES

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ABSTRACT

A number of high temperature industrial processes offer temperature, mixing and a gaseous residence time condition which may be sufficient to thermally destroy hazardous wastes of various types. Industrial boilers and cement kilns are most often considered for this purpose. Incineration in lime kilns, steel making furnaces and other processes may also be technically feasible and economically attractive. Consideration must be given, however, to the physical form of wastes, firing methods, residue handling, air pollution control, "incinerability" of the waste and compatibility of the waste material with the industrial process of interest.

SUITABILITY OF OPEN HEARTH FURNACES FOR DESTRUCTION OF HAZARDOUS WASTE

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ABSTRACT

The high temperatures and retention times achieved in open hearth furnaces suggest their consideration as candidates for destruction of hazardous wastes. Conceptually, liquid wastes could be co-fired with fuel in the burners and semisolid and solid wastes could be charged into the furnace. A particularly difficult problem in present hazardous waste destruction is the disposal of contaminated drums. Complete cleaning is expensive and time consuming. Destruction of contaminated drums and other solid wastes is an opportunity not offered in many other destruction schemes.

Serious complications coexist with the advantages of this concept. Control of fugitive emissions, explosion hazards, and potential worker exposure are among the problems to be evaluated. It appears unlikely that hazardous waste destruction could be accommodated in an ongoing steel

making operation. An alternative is the conversion of an abandoned furnace to serve primarily as a destruction operation with the production of low-grade steel as a by-product. Economics will dictate the ultimate viability of such an approach as site cleanup activities proceed over the next five years under the Superfund program.

SUITABILITY OF BLAST FURNACES FOR DESTRUCTION OF HAZARDOUS WASTES

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ABSTRACT

The potential for the injection of hazardous wastes in the tuyeres of a blast furnace is discussed in terms of the thermochemical conditions that exist in the raceways and smelting zone of an operating blast furnace. The temperature in the tuyere zone of a blast furnace is approximately 2121°C (3850°F). As the preheated air with additives enters the furnace through the tuyeres, the chemical potential of oxygen rapidly decreases because of the excess supply of hot coke. Hence, the conditions are characterized by high-temperature (>2000°C), strong reducing potential $P_{O_2} < 10^{-20}$ atm), and moderate pressure (<10 atm). Under such conditions, many hazardous materials may be dissociated into simple molecules. Currently, tars, oils, and pulverized coals are injected in the tuyeres. Hence, a technology for tuyere injection is well developed. During the presentation, the fate of injected hazardous wastes, e.g., P.C.B., and the potential effects on blast furnace operations are discussed.

Session 3: WATER POLLUTION ABATEMENT

Chairman: Terry N. Oda
Region III
U.S. Environmental Protection Agency
Philadelphia, PA

MINIMIZING RECYCLED WATER BLOWDOWN FROM BLAST FURNACE GAS CLEANING SYSTEMS

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Cleveland, OH 44101

ABSTRACT

Retrofit water recycle systems were put in operation late in 1976 on the gas cleaning systems for two blast furnace complexes located at Republic Steel Corporation's Cleveland District steel making facility. Since the start up of these systems, efforts have been made to reduce blowdown by identification and elimination of extraneous water sources. The overall effect of these efforts has caused significant changes in constituent loadings from these systems to the receiving stream, the Cuyahoga River. Recently, the goal of blowdown reduction has shifted to the elimination of discharge to the river, with efforts directed toward continued operation of a very "tight" recycle system. Long-term effects are yet to be resolved.

The paper maps the development of a blast furnace treatment facility from "once through" to "recycled" with a low blowdown rate. Current work concerning the continuous operation of a tightly closed recycle system is presented. This includes maintaining hydraulic balance, monitoring water chemistry and feeding different treatment chemicals to control potential problems associated with highly cycled water. It also presents a pictorial display and schematic representation of the system, and a graphic analysis of key parameters and water quality trends.

Finally, the paper focuses on studies conducted jointly by Republic Steel and USEPA on one of the recycle water systems. This was accomplished with the use of the USEPA Mobile Treatment System - Trailer No. 1 during the spring and summer of 1981. Initial work included testing on a pilot plant scale (5-6 gpm) of softening a portion of the recycle stream. Secondary work investigated proposed BAT/BCT Alternate #4 (Alkaline-Chlorination) for blowdown treatment from a very highly cycled blast furnace recycle system.

BACKGROUND

Republic Steel Corporation's Cleveland District is an integrated steel making facility located along the Cuyahoga River in Cleveland, Ohio. Its principal products are bar, hot band and cold roll strip. The facility includes four blast furnaces, two coke plants, a two vessel B.O.F. shop, billet mill, slabbing mill, bar mills, and a hot and cold rolling mill complex. Blast Furnace Nos. 5 and 6 are one of two separate basic iron making complexes, the other being Blast Furnace Nos. 1 and 4.

Blast Furnace No. 5 was originally constructed as part of the Defense Plant Corporation and was put in operation in 1943. No. 6 Blast Furnace was added in 1952 as a sister furnace to complete the complex. Both furnaces have similar statistics, with hearth diameters of 29'-6" and working volumes of slightly over 56,000 cubic feet. Both produce basic iron and are burdened primarily with pellets, some ore and roll scale depending on stock availability and clean water quenched coke. They each have a maximum wind rate of 125,000 SCFM, with combined production capability of approximately 5,600 tons per day.

Original equipment gas cleaning systems were replaced and modified so that each system now consists of a dry dust catcher, primary scrubber, primary separator, secondary scrubber, flooded elbow and spray type gas cooler. The original water treatment facility, built in 1943, consisted of one 120' diameter thickener with related pumping and filtering equipment. This thickener system was replaced in 1972 with the present water treatment plant. The "once through" treatment plant was designed to treat water from the gas cleaning system with the effluent discharged to the Cuyahoga River.

The treatment plant consists of a scalping pit, influent sump with three low lift vertical slurry pumps, rapid mixing tank, two 90' diameter reactor-clarifiers, three disc type vacuum filters for sludge dewatering, chemical feed systems for lime and ferric chloride, and other ancillary pumping systems. This plant effectively functioned as a once through system until November, 1976 when the recycle portion of the facility was completed and added to the operation.

The recycle system includes a pH adjustment tank, hot well with four vertical slurry pumps, five cell spray type cooling tower, cold well with four return water supply pumps, make-up sump with two vertical pumps, three chemical feed systems, control and recorder console, and other auxiliary systems. At the blast furnaces, the recycled water supply was tied into the existing gas cleaning system supply, replacing once used non-contact cooling water (Cuyahoga River water) as the medium for gas cleaning and cooling. As shown in Figures 1 and 2, the treated recycle water is fed to each gas cooler, with a portion of the gas cooler effluent recycled to the primary and secondary scrubbers. This contact water is then collected and directed through a dirty water return trench to the treatment plant for solids removal, cooling and recycle back to the gas coolers (Figure 3).

Each furnace has adjacent dual section slag pits. Slag is primarily air cooled, with spray systems used for final quench prior to solidified slag removal by a contractor. The quench system on No. 6 furnace is a recirculating type with runoff collected in a sump, supplemented with make-up, then resprayed on the hot slag (Figure 4). The final runoff volume at conclusion of the quenching operation is blown down to the treatment plant.

Various effluents from No. 2 Powerhouse, which services this blast furnace complex, are also directed to the treatment plant. These effluents

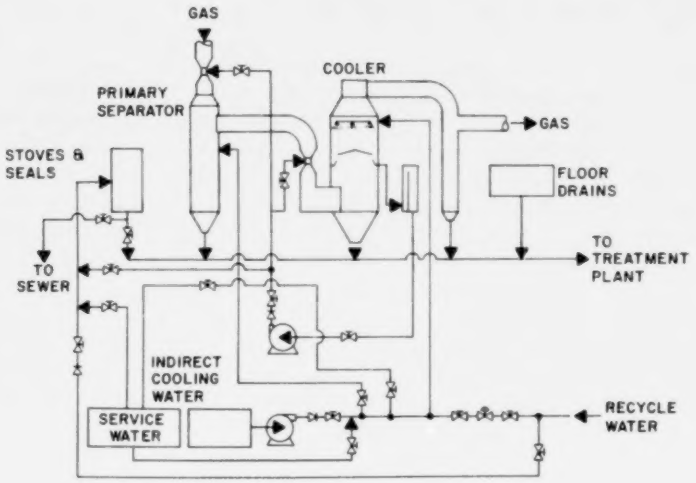
GAS
PRIMARY SEPARATOR
COOLER
GAS
STOVES & SEALS
FLOOR DRAINS
TO TREATMENT PLANT
TO SEWER
INDIRECT COOLING WATER
SERVICE WATER
RECYCLE WATER

Figure 1. Republic Steel Cleveland District - No. 5 Blast Furnace Gas Cleaning System Flow Schematic.

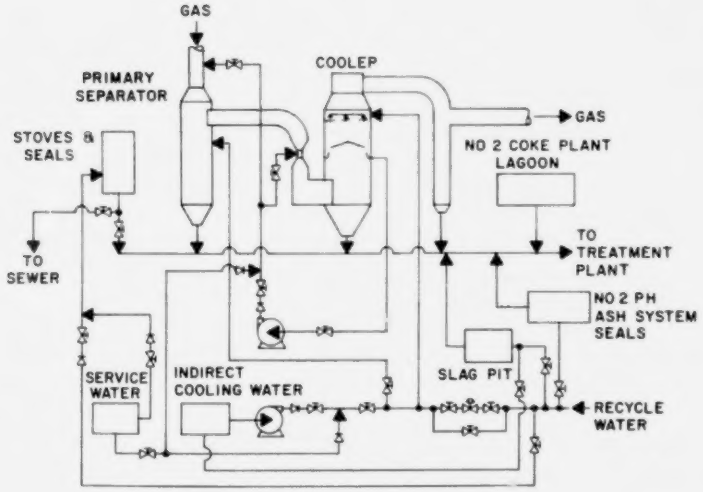
GAS
PRIMARY SEPARATOR
COOLEP
GAS
STOVES & SEALS
NO 2 COKE PLANT LAGOON
TO TREATMENT PLANT
TO SEWER
NO 2 PH ASH SYSTEM SEALS
SLAG PIT
SERVICE WATER
INDIRECT COOLING WATER
RECYCLE WATER

Figure 2. Republic Steel Cleveland District - No. 6 Blast Furnace Gas Cleaning System Flow Schematic.

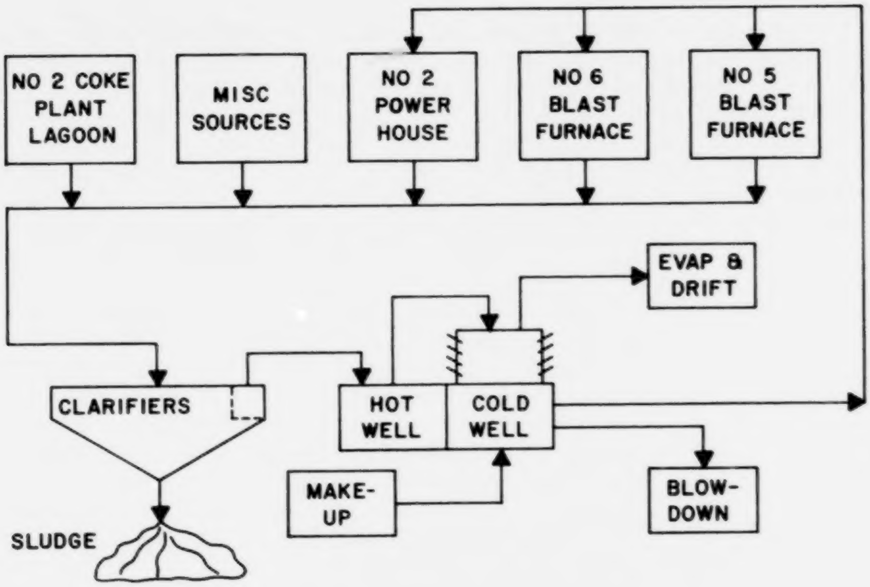
NO 2 COKE PLANT LAGOON
MISC SOURCES
NO 2 POWER HOUSE
NO 6 BLAST FURNACE
NO 5 BLAST FURNACE
EVAP & DRIFT
CLARIFIERS
HOT WELL
COLD WELL
MAKE-UP
BLOW-DOWN
SLUDGE

Figure 3. Republic Steel Cleveland District - Flow Schematic for Nos. 5 and 6 Blast Furnace Gas Cleaning Water Recycle System.

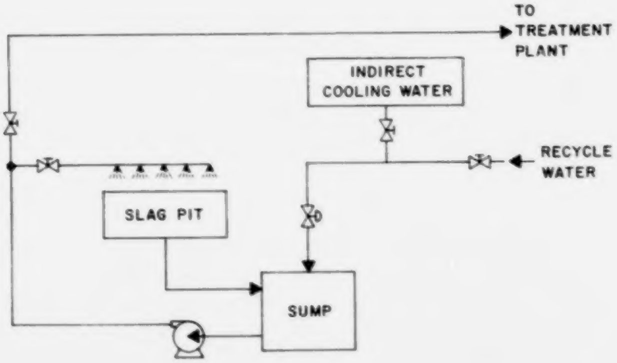
TO TREATMENT PLANT
INDIRECT COOLING WATER
RECYCLE WATER
SLAG PIT
SUMP

Figure 4. Republic Steel Cleveland District - Typical blast furnace slag pit recirculation system.

consist of miscellaneous seals and boiler drains and discharge from the boiler fly ash collection and removal system.

SYSTEM HYDRAULICS

The recycle system supplies approximately 8,200 gpm to the blast furnace gas cleaning systems. No. 5 gas cooler receives about 3,600 gpm and No. 6 gas cooler approximately 4,000 gpm, with the balance pumped to primary separator sprays and miscellaneous seals. These flows vary depending on furnace operations, wind rate and recycle water temperature. Initial design of the recycle system targeted a blowdown rate of 1,000-1,200 gpm, to be controlled by conductivity of the system. In order to better control blowdown flows and discharge loads, the conductivity control was converted to flow control of blowdown with continuous monitoring of system conductivity.

It became apparent that system blowdown rate was dictated by hydraulic imbalance rather than high conductivity. This condition of hydraulic imbalance in a recycle system is not at all uncommon, especially in retrofit systems such as those on Republic's two blast furnace complexes. Applying the methodology of a flow balance, where incoming and discharge flows are compared, was the approach used to solve this hydraulic problem. Major or obvious sources of incoming extraneous water were identified and plans were developed to eliminate them. As investigations continued, identification of other sources became more difficult, as did the solutions.

REDUCTION OF BLOWDOWN

Establishing the flow balance of the system became the tool for illuminating various problems. Progress of these efforts was monitored by comparing blowdown flow to the controlled make-up flow at the recycle system. Blowdown flow was continously reduced to minimize the need for controlled make-up.

In most cases, there was no easy way to identify the sources. As with most operating units, the years tend to complicate an already intricate system of piping and valving with cross connections, contingency back up and surreptitious routing of piping throughout. Precautions were taken on the piping system evaluation by monitoring line pressure to assure direction of water flow at varous tie-in points. The use of dye, both visually and in conjunction with a fluorimeter proved to be a valuable aid.

NO. 2 POWERHOUSE

The single major source of extraneous water into the recycle system was from the fly ash removal and sluicing system for the boilers at No. 2 Powerhouse. This system had been discharging to the treatment plant for suspended solids removal since the treatment plant was built. To eliminate this as an extraneous water source, the ash sluice system was made a part of the entire recycle loop by replacing service water supply with recycle water supply (Figure 5). This approach of converting extraneous water sources with recycle water when they cannot be diverted from the treatment system became the most important step in solving hydraulic imbalance problems.

When the ash sluicing system was tied into the recycle loop, recycle water became available in the powerhouse. Various gas seals which drained to the recycle system were converted to recycle water supply, as was a sump eductor that had been supplied with city water. Tie-ins to existing powerhouse piping became potential sources of water loss from the recycle system. This problem was corrected by valve identification and tagging. Boiler blowdown and zeolite softener backwash and rinse water, both high in

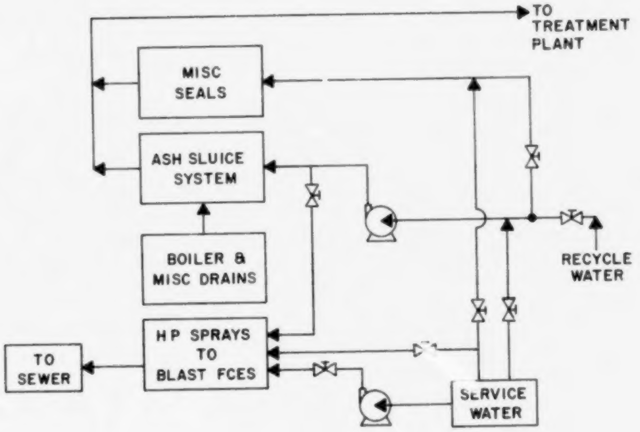
TO TREATMENT PLANT
MISC SEALS
ASH SLUICE SYSTEM
BOILER & MISC DRAINS
HP SPRAYS TO BLAST FCES
TO SEWER
RECYCLE WATER
SERVICE WATER

Figure 5. Republic Steel Cleveland District - No. 2 Powerhouse Flow Schematic.

dissolved solids, were diverted from the recycle system.

NO. 5 BLAST FURNACE

Service water ties to back up pumps for the recycle water supply were identified and shut. Some cast house floor drains were also found to discharge to the recycle system. Although this problem has not yet been resolved, it is known to be an extraneous source. Recently, with the deteriorating physical condition of this furnace as it concludes its present campaign, turn down tuyere water to these drains has increased the hydraulic imbalance in the system.

NO. 6 BLAST FURNACE

When this furnace was down for lining repairs in 1979, identified extraneous water sources were eliminated. The alternate service water connection to the recycle water supply was routed to the cast house area, identified, tagged and shut. Indirect cooling water from a section of a furnace cooling circuit was discharging to a drain at the cast house. This drain was rerouted from the recycle system to the indirect cooling water discharge sewer. The slag pit quench system became another extraneous source when shutdown and drained to the recycle system. Service water make-up for slag quench was replaced with recycle water to eliminate this source.

BLAST FURNACE STOVE VALVE COOLING

In the past, Republic Steel's Cleveland District Blast Furnaces have experienced problems with valve cooling on the stoves due to the occasional high silt loadings of Cuyahoga River water during and after rain storms. Looking at the consistently high quality of treatment plant effluent convinced the blast furnace operators that application of recycled water for stove cooling would solve this silt problem. Unfortunately, simultaneous tightening up of the recycle system changed the water chemistry by dramatically increasing calcium carbonate scaling on the heat transfer surfaces. After several piping changes and unsuccessful combinations of recycle and service water on the stoves, with service water causing hydraulic imbalance, the decision was made to return to service water for stove valve cooling water discharge sewer.

TREATMENT PLANT

Several small sources of extraneous water were identified at the treatment plant, all of which involved the use of city water for bearing lubrication, packing gland seals or water ring compressor seals and cooling. Consideration has been given to further treat recycle water as a city water replacement for these applications. A potential water loss was the sump overflow for the high pressure flushing pump which discharges to the river. This accounted for occasional discrepancies in the hydraulic balance of the system. The source of water for this sump is clarifier effluent, so casual control of the sump level allowed for a recycle water loss at the overflow. The permanent solution is relocation of the high pressure pump to the cooling tower cold well. Until this is completed, monitoring of sump level while the pump is in use prevents the overflow and subsequent water loss.

The make-up butterfly control valve was found to be leaking due to a torn seat. This problem was easily corrected by changing the seat material from viton to teflon.

INSTRUMENTATION EFFECTS

The entire process of monitoring the hydraulic balance, essential in reducing blowdown to any desired level, was dependent on information provided by system instrumentation. The accuracy and reliability of flow monitoring and control loops must be stressed. An incorrect flow or level indication can cause false conclusions to be drawn about system status.

Flexibility of instrumentation provided tighter control and more accurate analysis of the system hydraulics. Original blowdown control based on conductivity measurement was changed to blowdown flow control to better track the system hydraulics. Later, this flow control was "biased" by the addition of cold well high level control which allowed for blowdown of only extraneous water from the system. By set point adjustment of blowdown flow, make-up control and "bias" blowdown based on cold well level, minimum make-up, minimum blowdown and maximum surge capacity in the cooling tower wells were established.

HYDRAULIC BALANCE

Other factors considered in establishing the hydraulic balance for this system were water pick-up in gas cleaning and cooling from furnace operation, water loss at the cooling tower and the concept that the recycle system is not a terminal treatment plant.

Water pick-up at the furnaces is due to burden moisture, blast moisture, reaction water and possible water infiltration due to leaks in furnace cooling members. This water is condensed as the gas is cooled from furnace top temperature (300-400° F) to gas cooler temperature (80-90° F), and at this blast furnace complex is estimated to be 70-75 gpm per furnace.

Cooling tower losses due to evaporation and drift also vary due to operating and atmospheric conditions and cooling tower design. Applying an estimated cooling tower evaporation rate of 1% of recirculation rate per 10° F of temperature differential, an estimated average of 250 gpm was established for this system. The net effect of these factors yielded the ability of the system to eliminate about 100 gpm of extraneous water.

Applying the rational that the recycle system is not a terminal treatment plant, a potential extraneous source from the adjacent No. 2 Coke Plant was averted. Blowdown from the gas scrubber system on a recently installed one spot coke quench car was to be directed to the treatment plant for suspended solids removal. By maintaining solids removal capability at the quench station, this blowdown was directed to coke quench.

As seen in Figure 6, blowdown flow has steadily decreased since initial

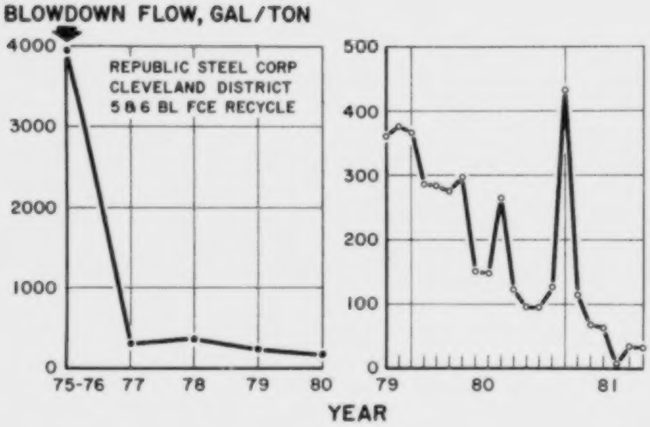

Figure 6. Republic Steel Cleveland District - Nos. 5 and 6 Blast Furnace Recycle System - Blowdown flow by year.

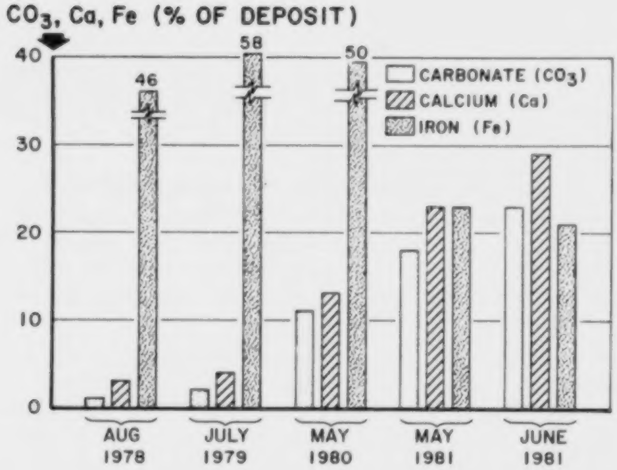

Figure 7. Republic Steel Cleveland District - Nos. 5 and 6 Blast Furnace Recycle System - Deposit analyses history.

start up of the recycle system in late 1976. Recent efforts of operating hydraulically at zero blowdown have been achieved only for short periods of time because of known extraneous water from No. 5 Blast Furnace which includes turn down water and external shell spray cooling. For this sytem, a sustained very low blowdown rate is hydraulically achievable and has been demonstrated. However, long-term operation at a low blowdown rate seems possible only with optimum conditions throughout the entire system.

CONTINUOUS OPERATION AT LOW BLOWDOWN FLOW

WATER CHEMISTRY CHANGES

As blowdown rates were decreased, system data supported predicted trends. Figure 8 shows the increase in concentration of total dissolved solids as the system cycled up. Each point represents a yearly average of weekly samples composited over a 24-hour period. The 1975-76 average is for once through treatment, prior to recycle. The upward trend graphically portrays the cycling up of various dissolved constituents as system hydraulic balance improved and subsequent blowdown rate decreased.

The result of a more pronounced decrease in blowdown from November, 1979 to July, 1981 is demonstrated by increasing trends of total dissolved solids, total hardness and total alkalinity as shown in Figure 9. Each trend curve represents a best fit of data statistically significant with 99% confidence. During this period, the monthly average of blowdown rate was as low as 8 gallons per ton, and for several short periods, there was zero system blowdown. While at near zero or zero blowdown, system water conductivity increased to the 7,000-8,000 micromho range, with total hardness concentration of 1,000-1,400 mg/l.

The nature of deposits throughout the system also showed marked change in characteristics. Results of deposit analyses over a period of time (Figure 7) illuminate the change from material high in iron to a deposit high in calcium carbonate.

TREATMENT CHANGES

Initial water treatment of the once through system, prior to recycle, concentrated primarily on water clarification for suspended solids removal. A combination of cationic polymer for particle charge neutralization, anionic polymer for suspended solids removal and ferric chloride for clarity was used. On start up of the recycle system, basic water clarification treatment was supplemented with a combination dispersant product, with a surfactant for particle wetting, polymer for solids carryover and lignin as an iron dispersant. As the recycle system was tightened up, deposit analyses indicated a need for improvement in deposit control, focusing on iron deposition was well as calcium carbonate scale. The use of ferric chloride was discontinued to reduce the input of dissolved iron into the system. Additionally, reduced blowdown flows minimized the need for very high clarity water. The high conductivity of the system water indicated a higher particle charge, necessitating changes in both cationic and anionic polymers.

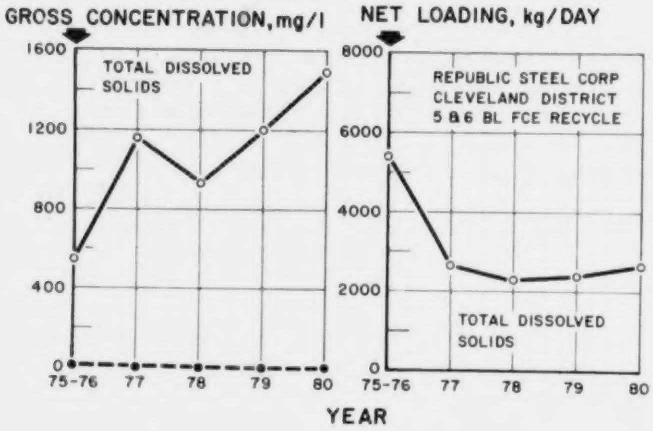

Figure 8. Republic Steel Cleveland District - Nos. 5 and 6 Blast Furnace Recycle System - Total Dissolved Solids gross concentration and net loading to discharge by year.

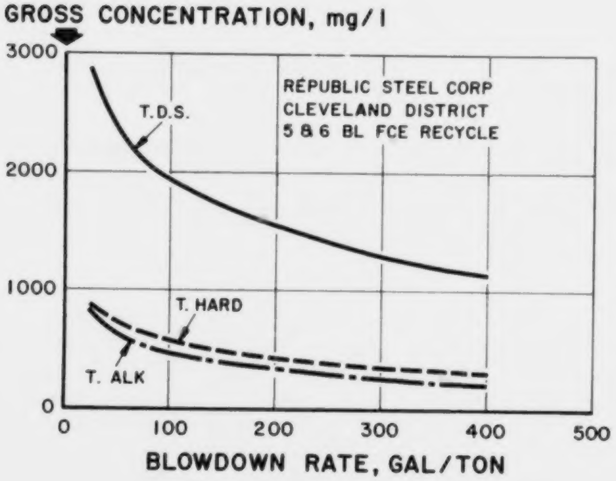

Figure 9. Republic Steel Cleveland District - Nos. 5 and 6 Blast Furnace Recycle System - Total dissolved solids, total hardness and total alkalinity concentration as a function of blowdown rate (November 1979-July 1981).

Most recently, deposit analyses and water chemistry trends have magnified the need for a change from an anti-foulant to a product which was a more specific inhibitor for calcium carbonate deposition. Throughout this process of tightening up the recycle system, constant emphasis was placed on the need for controlling the potential for deposition which could lead to operating problems at the treatment plant and the blast furnaces. The water treatment supplier directed their efforts for minimizing this deposition potential. Their responsiblity was to keep the system out of trouble as near zero or zero blowdown was hydraulically approached.

Increased activity with sampling and monitoring followed. Procedures were set up for daily analyses by the plant operators for conductivity, total hardness, calcium hardness, alkalinity and chloride concentrations in the recycle and make-up water. Deposition and corrosion coupons were installed at key locations throughout the system, including recycle supply line, blast furnace cooler supply lines, inside the blast furnace coolers and in the scrubber supply lines.

INSPECTIONS

The frequency of internal gas cooler inspections was increased to supplement the ongoing sampling and monitoring. The primary objective was to detect and track changes inside the gas coolers, which provided a full scale demonstration of water chemistry and treatment effectiveness. The most obvious observation was the plating out of a thin calcium carbonate layer over the entire wetted portion of the upper section of the gas coolers. The appearance was as if the inside had been spray painted. This area had previously shown signs of corrosion, due to the depressed pH of the water caused by carbon dioxide absorption. The carbonate coating had covered previously detected areas of corrosion on side walls, grating, beams and nozzle piping. Inspection of internal cooling checkers did not reveal evidence of significant scaling to cause restriction in gas or water flow.

Inspection of deposit coupons in the system has shown no evidence of major deposit problem. There are indications that corrosion and/or erosion continues to be a potential problem, with some coolers showing "pitting" corrosion in internal members. Based upon inspections, it seems possible to have both calcium carbonate deposition and corrosion occurring simultaneously inside the coolers.

MAINTENANCE OF HYDRAULIC BALANCE

Daily maintenance of the system hydraulic balance continues to be a difficult task at extremely low blowdown rates. The large number of potential sources for gaining and losing water throughout the system requires a thorough knowledge of its physical layout. Preferably, the water treatment plant supervisor should be familiar with blast furnace, coke plant and powerhouse areas to locate and take action to correct hydraulic imbalance expeditiously.

More occurrences of hydraulic imbalance have surfaced due to the declining physical condition of No. 5 Blast Furnace than had occurred since recycle system start up. The operation of a blast furnace changes throughout its campaign, cycling every 4 to 5 years. The opportunity to make major modifications to correct hydraulic imbalance usually occurs only once every cycle, when the furnace is down for reline. Problems must be correctly identified and solutions applied at these times.

There were several indicators for monitoring system tightness, including water sampling and lab analysis. But correction of hydraulic imbalance to maintain very low blowdown had to be quickly remedied and, therefore, readily detected. This very tight system will lose more water through evaporation and cooling tower drift than it picks up from the blast furnace process. Therefore, make-up is required. Extraneous water sources in the system became uncontrolled sources of make-up. As long as these sources did not exceed the volume of water loss, the system remained in hydraulic balance. If these sources were less then system water loss, additional make-up had to be provided at controlled rate to maintain system water volume.

Monitoring controlled make-up flow indicated when the system was picking up extraneous water. At any given blowdown flow, if make-up flow decreased, the system was checked for extraneous water infiltration. If make-up flow increased, a check was made for water loss. In either case, chemical equilibrium of the system changed and was detected as a gradual change in conductivity.

At zero blowdown, monitoring of the system hydraulics became even more critical. For this recycle system extraneous water showed an increase in cold well level. When surge volume was consumed, this extra water was automatically blown down.

WATER CONSTITUENT TRENDS

Effects of cycling up the recycle system are graphically portrayed in the analyses of three prime constituents; ammonia, cyanide and phenol. Data collected on these constituents tracks the gross concentration and net loading annually from 1975 to 1980. More recent data, (November, 1979 to July, 1981) reveals the increaed concentrating effect of decreased blowdown. These constituent trends displayed a 99% confidence when statistically analyzed.

Ammonia Concentration

As seen in Figure 10, the increase in ammonia concentration, although not steady, was significant. The increased concentration was offset by decreased blowdown flow, yielding an overall net decrease in the ammonia load discharged. Analysis of recent data (Figure 13) shows a very sharp increase in ammonia concentrations as very low blowdown rates were achieved.

The concentration of ammonia is dependent on several other factors, with the type of water used for coke quench being very significant. The majority of coke used in these blast furnaces has been quenched with river water or treated process effluent from a physical chemical treatment plant at the No. 1 Coke Plant. Stripping of ammonia throughout the system (clarifiers, launders and cooling tower) is also to be considered, as is system pH which determines

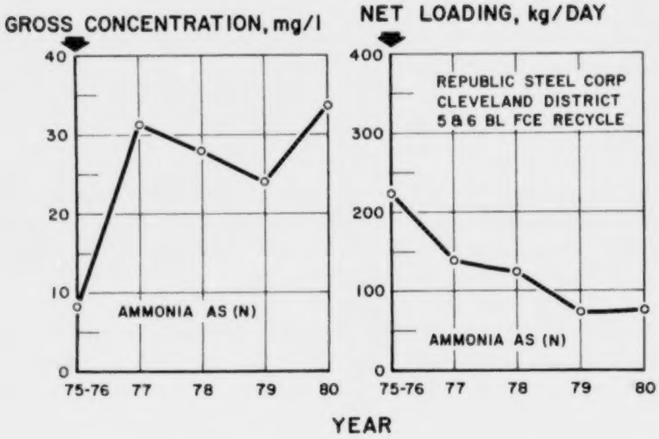

Figure 10. Republic Steel Cleveland District Nos. 5 and 6 Blast Furnace Recycle System - Ammonia gross concentration and net loading to discharge by year.

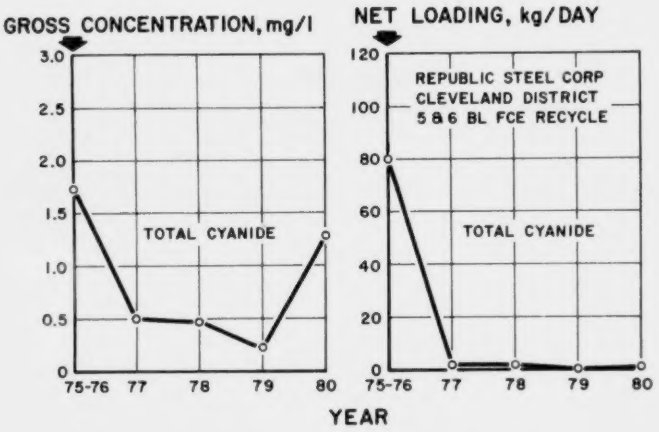

Figure 11. Republic Steel Cleveland District Nos. 5 and 6 Blast Furnace Recycle System - Total Cyanide gross concentration and net loading to discharge by year.

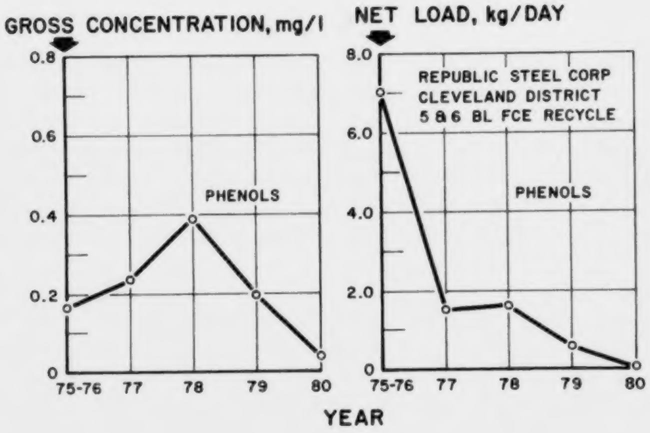

Figure 12. Republic Steel Cleveland District Nos. 5 and 6 Blast Furnace Recycle System - Phenol gross concentration and net loading to discharge by year.

the absorptive capacity of the water for the gas. The net effect is that ammonia concentration has reached relatively high levels (100-200 mg/l) when the blowdown was reduced to very low levels.

Cyanide and Phenol Concentration

The results of decreasing blowdown do not indicate consistent long-term trends for cyanide and phenol concentrations (Figures 11 and 12). These constituents apparently are more process related. The net loading does show a drastic reduction, again due to the reduced blowdown rate.

However, analysis of data during significant blowdown reduction (Figures 14 and 15) display the same concentrating trend at very low blowdown rates. The effect of cyanide stripping in the system becomes part of this net effect.

ONGOING CONSIDERATIONS

Efforts toward blowdown reduction were initiated to improve the overall efficiency of the recycle system and to decrease the net loading discharge of various constituents. The January 7, 1981 proposed effluent standards for BAT/BCT technology indicate two alternatives of treatment, zero discharge or additional treatment of blowdown prior to discharge. For zero discharge, hydraulic balance is absolutely essential to eliminate the need to hydraulically dispose of water. For additional treatment of the blowdown discharged, capital and operating expenditure for a treatment scheme can be reduced by minimizing the flow rate.

SIDE STREAM SOFTENING

Confirmed by physical inspections, and as seen graphically in Figures 7 and 9, calcuim carbonate scaling is a potential problem as the system approaches zero blowdown. Continued performance or cost effectiveness of chemical treatment to cope with this potential is untried and unknown. The decision was made to examine the possibility of transferring side stream softening technology to the blast furnace recycle system.

With the aid of the USEPA Mobile Pilot Treatment Plant, a comprehensive study of the use of water softening chemistry was undertaken. The intent was to investigate various chemical modes on a 5-6 gpm side stream to determine the feasibility and cost projections of side stream softening to control system hardness. The modes investigate were the use of lime, caustic, lime-soda ash and caustic-soda ash. Also investigated were the effects of recombination of the softened side stream with the unsoftened system water.

The pilot plant equipment included a rapid mix tank, flocculator and clarifier. A final filter was added to determine carryover of solids. The softening operation was determined by jar testing, then pilot plant results were applied to jar test data to verify the use of those tests in projecting softening reactions. The initial study was conducted on clarifier effluent.

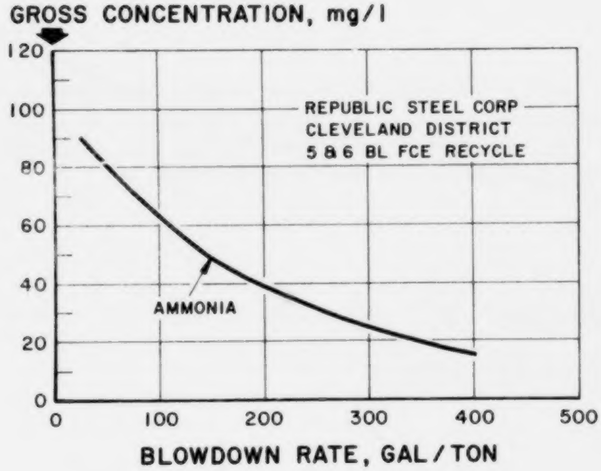

Figure 13. Republic Steel Cleveland District - Nos. 5 and 6 Blast Furnace Recycle System - Ammonia gross concentration as a function of blowdown rate (November 1979-July 1981).

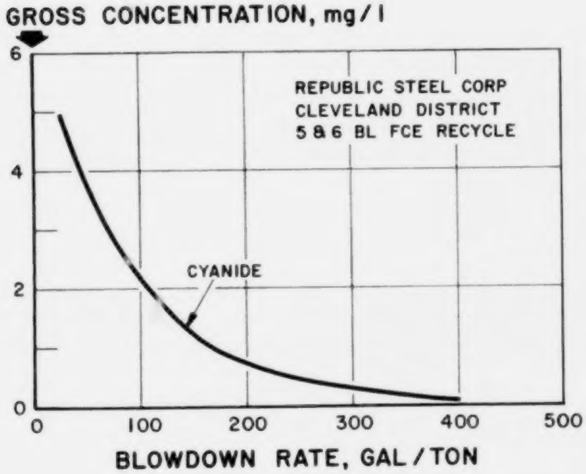

Figure 14. Republic Steel Cleveland District - Nos. 5 and 6 Blast Furnace Recycle System - Total Cyanide gross concentration as a function of blowdown rate (November 1979-July 1981).

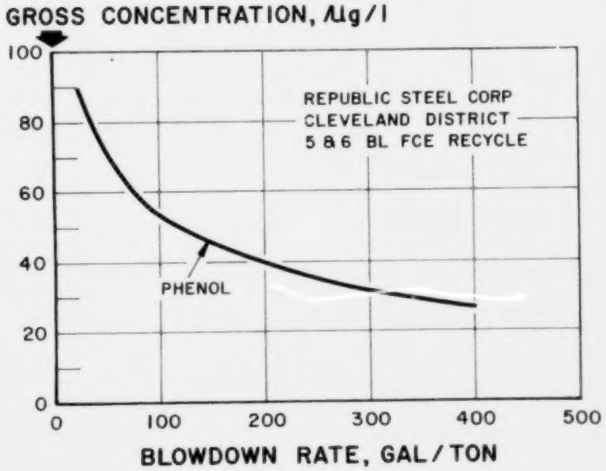

Figure 15. Republic Steel Cleveland District - Nos. 5 and 6 Blast Furnace Recycle System - Phenol gross concentration as a function of blowdown rate (November 1979-July 1981).

Lime Softening

With the use of lime only for softening, there was a slight decrease in total hardness. At elevated pH values, magnesium hardness was significantly reduced, only to be replaced by calcium hardness, lime being the calcium donor. Thus, the net total hardness decrease was not significant.

Caustic Soda Softening

By elevating the pH with the use of caustic, dramatic decrease in both magnesium and calcium hardness occurred. This reduction in total hardness optimized in a range of 10.5-11.0. There apparently was sufficient carbonate present in the water to precipitate out most of the calcium. This was accompanied by a slight increase in total alkalinity, but only significant at pH values over 10.0.

Lime-Soda Ash Softening

The increased calcium hardness with the use of lime only was eliminated with the addition of soda ash at elevated pH values. The carbonate donor soda ash significantly reduced total hardness and precipitated calcium carbonate. As total hardness reduction optimized, total alkalinity started increasing due to the then excess carbonate. This represented a somewhat classic lime-soda ash softening process.

Caustic Soda Ash Softening

At higher pH values, the addition of soda ash served no value, as sufficient carbonate was already present in the water for precipitation of calcium. Adding soda ash had little effect on total hardness reduction, and only increased total alkalinity.

Remixing of Softened With Unsoftened Water

Of particular concern with side stream as opposed to full stream softening was the effect of remixing these streams. If the mixed water continued the softening reaction, precipitation of solids could create a sludge problem in areas where removal is difficult if not impossible without a major outage. Remixing of softened water from each softening process with unsoftened water indicated that calcium hardness decreased as the percent of softened water increased. Precipitation of solids did occur.

Other Softening Trials

Further tests were conducted to check softening reactions at points of the system other than the clarifier effluent. Trials of cold well effluent and dirty water influent parallelled results from the previous tests.

The pilot plant was operated with each softening method and the results compared to the jar test studies. Pilot plant lime softening reflected the jar test data. Caustic and caustic-soda ash softening in the pilot plant showed better results than did the jar tests. However, pilot plant lime-soda ash softening results were not as good as jar test indications. The reasons for this have not yet been determined, but should be investigated further.

Full Scale Trial

Based on results of these tests, costs of softening this water were projected for a full scale trial. These costs varied with the chemical used and ranged from $260 to $2,600 per million gallons treated, and are based on initial softening of the entire system. However, costs of maintaining the softening reaction can be put into perspective by comparing them to existing chemical treatment costs for clarification and deposit control at approximately $50 per million gallons treated.

Potential calcium carbonate scaling was overwhelmingly evidenced if efforts were to continue toward operating this recycle system with very low blowdown. Because side stream softening appeared as a viable means of controlling calcium carbonate scaling, the decision was made to proceed with a full scale trial. Plans for temporary modification of one of the two clarifiers to side stream soften treatment plant influent are underway as of this writing. The trial will commence with the use of caustic as the softening chemical. This method, although expensive, provides a less cumbersome approach during the trial to evaluate the total system effect. The objective is to determine if system hardness (calcium carbonate scaling potential) can be controlled by side stream softening, and to provide more detailed operating costs.

ALKALINE-CHLORINATION TREATMENT OF BLOWDOWN

Because of the ability of this blast furnace recycle system to achieve very low blowdown rates, it was decided to utilize the USEPA Pilot Plant facilities to further investigate the cost of blowdown for cyanide removal. As seen in Figures 13, 14 and 15, concentrations of ammonia, cyanide and phenol show a definite increasing trend as blowdown rates decreased. Specifically, the presence of ammonia can cause significant increase in chlorine demand before cyanide destruction can occur.

Preliminary results confirm that ammonia concentration is a major consideration in the alkaline-chlorination treatment scheme. Additional testing is underway as of this writing to further investigate air stripping as a supplemental means of ammonia reduction combined with alkaline-chlorination.

Acknowledgments

The authors wish to express their appreciation to Messrs. Gary Skerl and Kenneth Siegel of Republic Steel for their help in compiling and statistically analyzing the data. Also, we would like to thank Messrs. A. Crespo, G. Main and T. Medvin of Republic Steel's Research Center for the efforts they expended in making the figures and slides used for the speech and in the text of the paper. Finally, we would like to acknowledge Mr. M. Raymond Matuza of Betz Laboratories for his help in coordinating the many services provided by his company during this test.

MINIMIZING WATER BLOWDOWNS FROM SELECTED STEEL PLANT PROCESSES

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ABSTRACT

The objective of the project was to attempt to minimize the volumes of water blown down from:

- Blast Furnaces
- BOF
- Continuous Casters
- Hot Forming Mills
- Sinter Plants
- Electric Arc Furnaces
- Vacuum Degassers

while meeting the following constraints:

- existing treatment facilities to be used
- no major capital equipment to be used
- the reduction would have no adverse impact on the production facilities.

The methodology followed to perform the task was to:

A. Review existing literature to determine which plants have extensive recirculation systems installed and discharge volumes that are close to BAT volumes (October 1979 proposed guidelines).

B. Contact candidate plants, arrange to visit and present the proposed program and receive agreement to cooperate.

C. Receive plants' data, perform paper studies, visit the plants to establish gauging and sampling points.

D. Gauge flows and sample at selected points and, where applicable, perform treatability studies.

E. Interview operating personnel to determine water volumes and qualities required for efficient plant operation and criteria for blowing down water.

F. Establish modified operating procedures and/or design system modifications and minor additions. Prepare a preliminary report.

G. Discuss the report with plants and obtain their concurrence.

H. Plants make modifications.

I. Operate modified systems for a period of sufficient length to prove that systems can be operated with reduced blowdown and without adverse effects.

J. Prepare a final report for each plant.

The paper presented includes the status of the project up to the time of presentation.

OBJECTIVES

In September 1980 Hydrotechnic Corporation received a contract from the U.S. EPA to provide technical services to assist in demonstrating at steel plant sites that wastewater blowdown volumes from steel plant processes can be reduced to minimum levels with carefully controlled recycle systems. The steel plant processes selected by EPA were:

Basic Oxygen Furnace
Blast Furnace
Continuous Casting
Vacuum Degassing
Electric Arc Furnace
Hot Rolling Mill
Sinter Plant

The facilities to be selected for study were to be those that had, in place and operating, recycle systems that were not combined with other production process recycle systems. The selected system has to presently be discharging relatively low volumes of wastewater as blowdown. Additional constraints were that:

1. Recirculation and treatment facilities already in place were to form the basis for proposed discharge reductions.

2. There is to be no requirement for the addition of major capital equipment to accomplish the project goals.

3. Any reduction in flows discharged or any increase in recirculation rate would have no adverse impact upon the mill equipment or product quality.

METHODOLOGY

The first step in performance of the project was to select appropriate plants. A detailed review was made of the Draft Development Document for Proposed Guidelines (October 1979) and the data published in those documents were compared for accuracy against the original 308 data provided to EPA by the individual steel plants. In addition, trip reports written by the Development Document contractor were provided by EPA, in confidence, where additional data were available. Lists of candidate plants were then prepared. These lists were further condensed by eliminating individual plants that did not have multiple facilities of interest.

After the lists were prepared, a meeting was held between the contractor, EPA (Office of Research and Development, Research Triangle Park, NC), and the AISI. The purpose of this meeting, which was attended by various steel corporation representatives, was to explain the project objectives and to request the cooperation of the industry. The list of plants selected for the study was presented to the attendees during the presentation of the project description. If corporate representatives of the listed plants were present, their cooperation was requested.

Soon after the meeting, the appropriate companies were officially contacted and two plants with a total of six of the manufacturing facilities of interest (four at one plant and two at another) indicated a willingness to cooperate provided that they were given a more in-depth description of the work to be done and what was expected of their plant personnel. Subsequently, engineers from Hydrotechnic visited each of the plants to further explain the objectives of the project and define the plants' responsibility during the performance of the study. Both plants, after these presentations, agreed to host the study.

At each facility, existing data consisting of process flows within the system, treatment facilities in place and mode of operation, blowdown and makeup flows, qualities of water, production data and drawings (both flow and piping) were provided.

After study of the data, sampling and gauging locations were selected. A second trip was then made to each facility and, in the company of knowledgeable plant personnel, each sampling and/or gauging point was physically located and marked.

Most of the points were on pressure lines; therefore, Pitot tubes were used for flow measurement. Open channel flows were gauged with a Gurley current meter. The plants provided taps and valves on each of the lines of interest and, where necessary, uncovered points where flow measurements were to be made in open channels. Each plant also provided laboratory space where Hydrotechnic personnel performed routine analyses.

The survey consisted of gauging and/or sampling at each selected point at least two times.

After the surveys were performed, the data was analyzed and reduced and schematic flow diagrams were prepared for each production facility studied. Flow balances were made around each facility and the water quality deterioration, if any, was evaluated. Based on the data, water system modifications are to be developed and presented to the plants for their review. The purpose of this plant review is to check for accuracy of flow paths and to advise of any difficulties that might be encountered in implementing the suggested system modifications.

After consultation with the host plants, designs for implementation of the system modifications will be prepared and transmitted to the plant for installation of the required equipment and instrumentation. After installation, the system will be operated under the new conditions and monitored by Hydrotechnic engineers. Corrosion and deposition coupons will be inserted in the recirculation lines and measured periodically to determine the effects, if any, on the water systems. This discussion presumes that water application rates within the individual production processes are not changed; only the degree of recycle. It is not the function of this project to modify production operations which require specified amounts of water. However, if by making the mill personnel more water conscious, they may voluntarily reduce the quantities of water that are presently used. If this occurs, then it may be possible to reduce the volumes blown down by even greater amounts.

PRELIMINARY RESULTS OF THE STUDY

At one host plant, four different production processes water systems were studied: Blast furnaces; a B.O.F. shop; a continuous casting shop; and a secondary hot forming mill. The continuous casting shop has an electric furnace shop associated with it which utilizes dry gas cleaning. The host plant is presently reviewing the preliminary recommendations for the reduction of discharges that are based on this study.

In general it was found that the volume of blowdown in the systems studied is controlled by the amount of excess water that enters the systems at various points within the mills and shops. Operating personnel reported that no problems are experienced with the recirculated water quality returned for reuse from the respective treatment systems. At two mills operating personnel reported that the reason for adding makeup water at the mill was due to the inability of the recirculation system to return to the mill the volumes required for efficient operation.

A specific example of excess water entering a system is at the blast furnace water system. There are two operating blast furnaces with gas cooling and gas cleaning systems. Blowdown from the gas cooling system is cascaded to the gas cleaning system and the combined blowdown discharges from the gas cleaning system.

During the survey, gauging of the following was performed (Figure 1):

1. The flow from the gas cooling cold well.
2. The flow from the gas coolers to a settling basin.
3. The flow from the gas cooling hot well to the cooling tower.
4. Blowdown from the gas cooling system to the gas cleaning system.
5. Flow from the gas cleaning cold well.
6. Flow to the gas cleaning thickeners.
7. Flow from the gas cleaning hot well to the cooling tower.
8. Blowdown from the gas cleaning system.
9. Service water makeup to the gas cooling cold well.

The total system blowdown flow varied from 370 to 1000 gpm. Cooling tower losses were calculated to be 125 gpm and sludge hauling records indicated that the average daily sludge discharges contained approximately 55 gpm of water for a total system loss of from 550 to 1180 gpm.

Additions to the system of condensate from the blast furnace gas, estimated to be a maximum of approximately 165 gpm, and fresh water makeup, added to the gas cooling system cold well, amount to approximately 440 gpm.

Therefore, it can be seen that there is frequently more water blown down from the total system than can be accounted for by additions to the system.

We were informed that water from underground sumps, that accumulate ground water infiltration, is pumped into one or both of the water systems. It may, therefore, be possible to reduce the total blowdown caused by groundwater infiltration by reducing or eliminating the service water makeup and use this infiltration water as a total or partial source of makeup. Of course,. during dry weather periods, when infiltration is reduced, service water may have to be used for all makeup.

The positive Langelier Index calculated for the water in the gas cleaning system indicates a scaling tendency. However, no problems with scaling have been reported. Therefore, it is believed that by increasing the cycles of concentration, the system blowdown can be reduced. It is not known, nor is there a convenient way of measuring, the volume of seepage that enters the system; therefore, a guided trial-and-error procedure is being recommended for which blowdowns will be controlled by water level control in the gas cleaning system and by the effects on corrosion/deposition coupons, which would be inserted in the recirculating lines. These coupons will be inspected periodically. Based on this on-site, empirical

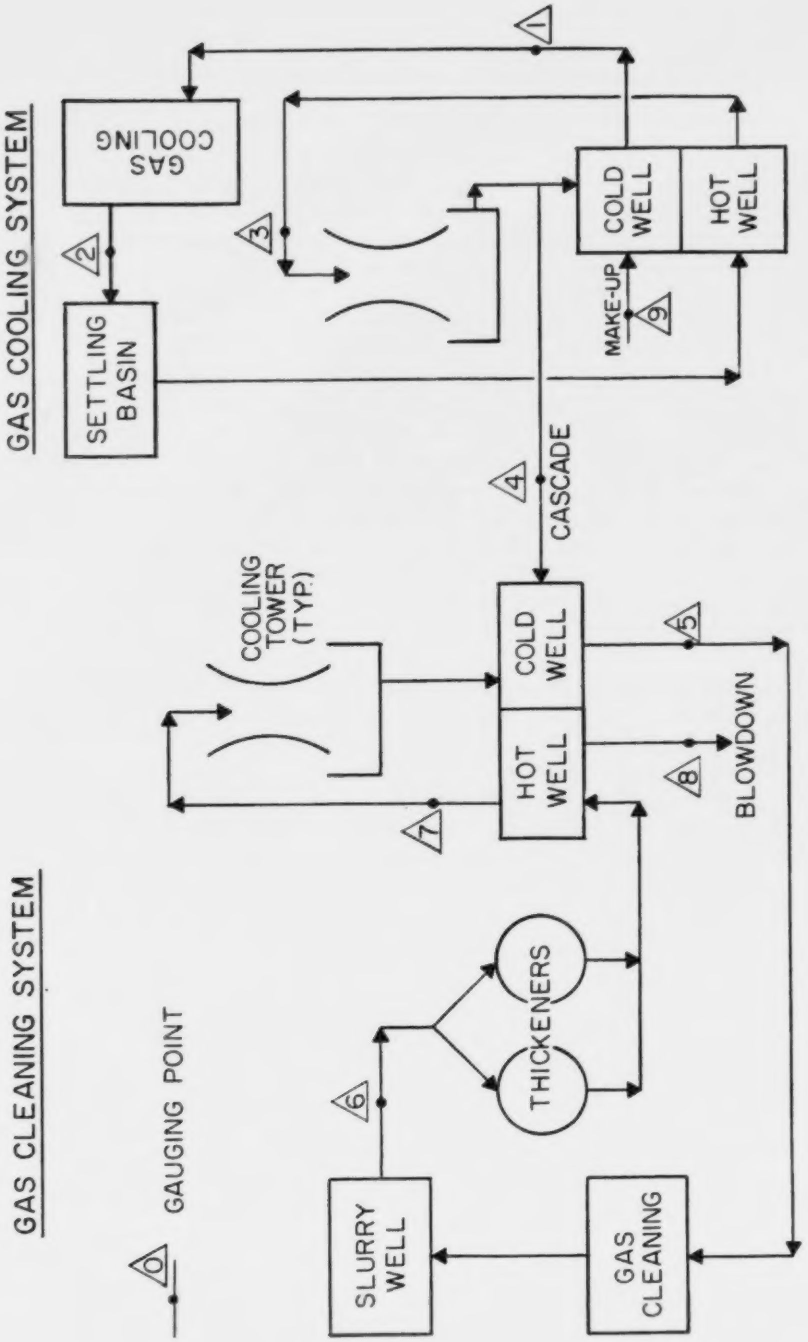
GAS COOLING SYSTEM
GAS COOLING
SETTLING BASIN
COLD WELL
HOT WELL
MAKE-UP
CASCADE
GAS CLEANING SYSTEM
GAUGING POINT
0
1
2
3
4
5
6
7
8
9
COOLING TOWER (TYP)
COLD WELL
HOT WELL
BLOWDOWN
THICKENERS
SLURRY WELL
GAS CLEANING

Figure 1. Flow Diagram Blast Furnace Water System

operation of the water systems over a period of 2-4 months, the actual amount of blowdown reduction can be ascertained. After this initial period, periodic checks are recommended to assure that long-time effects do not cause the water quality to further deteriorate to a point where an adverse effect is experienced either by the mill equipment or the product.

During this initial trial period and further test period, close coordination should be maintained with concerned plant personnel so that they are completely aware of what is happening; thus, when the test periods are completed, they are assured that the systems modifications as proposed do indeed produce lower blowdown volumes without affecting equipment or product and do not result in impractical cost increases.

CONCLUSIONS

Some reduction of discharges from production facilities can be accomplished by judicious water management, if operating personnel are kept aware of the fact that the quantities of wastewater discharged are of concern to plant and corporate management, not only with respect to meeting governmental regulations, but also with respect to the operating costs incurred when treating large volumes of wastewater. Wherever possible, recirculated water should be used. Introduction of extraneous water should be minimized. If this is not possible, as in the example cited, service or fresh water makeup should be reduced to take full advantage of the extraneous water as a source of makeup.

Mill operators should make it an ongoing effort to reduce water volumes to absolute minimums. In this manner it would be possible to reduce discharges with virtually no major capital expenditures. However, some in-mill repiping might permit further recirculation or reuse of water before treatment or cooling. Before these goals can be accomplished, plant personnel associated with the water systems must be convinced that the reductions are necessary and do not adversely affect the equipment or product.

ZINC CONTROL IN A BLAST FURNACE GAS WASHWATER RECIRCULATION SYSTEM

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ABSTRACT

In general, it is not possible to operate blast-furnace-gas-washwater circuits at a high degree of recirculation in a steel plant which also recycles a large proportion of zinc-containing scrap and solid wastes. Certain undesirable elements, particularly zinc, are not removed during iron- and steel-making, and will accumulate to dangerous levels under high recycle conditions.

The most serious danger is to blast furnace operations. Zinc threatens these operations by:

- endangering refractories (which can lead to blowout, collapse or premature shutdown of the furnace)
- causing the descending charge to stick (leading to operating irregularities, decreased furnace efficiency, and hazardous 'slips'), and
- depositing solids in water recirculating systems (which can block pipes and cause the collapse of cooling towers).

To avoid these problems, all steel companies restrict the amount of zinc in materials fed to blast furnaces. A typical maximum permissible level is 0.5 kg/tonne of iron produced - equivalent to about 0.02 percent of zinc in the raw materials fed to the furnace.

Stelco's Hilton Works in Hamilton, Ontario has an established practice of recycling solid wastes, including all blast furnace dust from both wet and dry collection systems. Severe operating problems were caused when a recirculation system was commissioned in 1978 for three blast furnaces which had previously operated with a once-through gas-washing and solids-separation system. Subsequently, it was found possible to operate, provided blast furnace dusts (up to 40 000 tonne/year) were dumped.

To avoid this disposal problem, a method of generating a zinc-laden blow-down stream has been devised, which enables zinc to be selectively purged from the system. This technique allows the water recirculation system to be operated, while still recycling most of the blast furnace dusts.

ABOUT STELCO

For the benefit of those unfamiliar with Stelco, the company is the largest steel producer in Canada. With an annual production capacity of over 6 million tonnes, Stelco produces about 35% of the nation's steel. Its operations are integrated from the mining of coal, iron ore, and limestone to the manufacture and distribution of iron, steel and steel products.

Stelco's manufacturing facilities comprise nineteen plants, located across Canada.

The main steel plant, Hilton Works, occupies 440 hectares, with harbor facilities in Hamilton, Ontario and is considered to be one of the most efficient integrated steel plants in North America. This high efficiency results in part from a long-standing emphasis on energy saving and the utilization of wastes.

RECYCLING OF WASTES

The steel industry has a strong tradition of recycling not only the wastes it generates itself, but also waste steel generated by the community. Scrapped steel products constitute a large proportion of the charge of steelmaking furnaces, from about 30 percent for BOF furnaces up to 100 percent for electric arc furnaces.

This tradition of waste recycling also extends to other solid wastes, especially those containing a high iron content, such as the iron oxide dusts collected by gas-cleaning equipment and the iron oxide scale formed during the heating and rolling of steel. These oxides are usually recycled to the blast furnace after agglomeration in a sinter plant.

But there are practical limits to the amounts which can be recycled. Some materials, including blast furnace flue dust and sludges, contain so-called "tramp" elements which are not removed in iron- and steel-making operations and which have undesirable effects on processes and products. Recycling of wastes containing such tramp elements leads to a successive build-up of the tramp elements in the processing system, causing deleterious effects on the process, or the production of unacceptable output.

Zinc is one tramp element of serious concern in steel manufacture, and it is usually associated with lead. Zinc and lead behave similarly, but zinc is usually present at higher levels than lead and so attention is normally directed to controlling it. The most serious effects of zinc and lead are on blast furnace operation.

EFFECTS OF ZINC AND LEAD ON BLAST FURNACE OPERATION

Serious operating problems result if zinc or lead is present in the raw materials charged to the blast furnace. The problems include:

- endangering the refractories (which can lead to blow-out, collapse or premature shutdown of the furnace);
- sticking of the descending charge (which can cause operating irregularities, decreased furnace efficiency, and dangerous "slips"); and
- deposition of zinc or lead compounds in water recirculating systems (which can block pipes and cause cooling towers to collapse).

Restriction of zinc and lead in materials fed to blast furnaces is practiced by steel companies throughout the world. A typical maximum permissible level is 0.5 kg of zinc/tonne of hot metal produced (equivalent to roughly 0.02 percent of zinc in the raw materials fed to the furnace).

Recycling of all blast furnace dusts from both wet and dry collection systems is a long-established feature of Stelco's operations. Although it is common practice in many steelplants to dump all or part of these wastes, at Stelco we recycle them all via a sinter plant to the blast furnaces. Control of zinc levels in the blast furnaces is therefore a continuing concern to our blast furnace operators.

EFFECTS OF RECIRCULATION OF BLAST FURNACE WASHWATER

Prior to 1978, three blast furnaces "B", "C" and "D", at Hilton Works in Hamilton operated on a "once through" washwater system. Water was pumped from Hamilton Bay to the gas coolers, scrubbers and wet precipitators. The water was then cleaned in thickeners, and returned to Hamilton Bay. All blast furnace flue dust and sludge filter-cake were recycled to the sinter plant feeding the blast furnaces.

Figure 1 schematically represents the zinc paths in the system under these once-through conditions. Zinc is present in the materials fed to the blast furnaces, notably in steelmaking slag (another recycled waste) and also in ore, fluxes and coke. Zinc is also present in the feeds to the sinter plant, most of which are recycled wastes such as blast furnace flue dust and filter cake, millscale, steelmaking fines and calcite-dolomite screenings. These zinc inputs to the system are balanced by zinc outlets from the system. The balance between zinc inputs and outputs determines the ultimate zinc level in the blast furnaces.

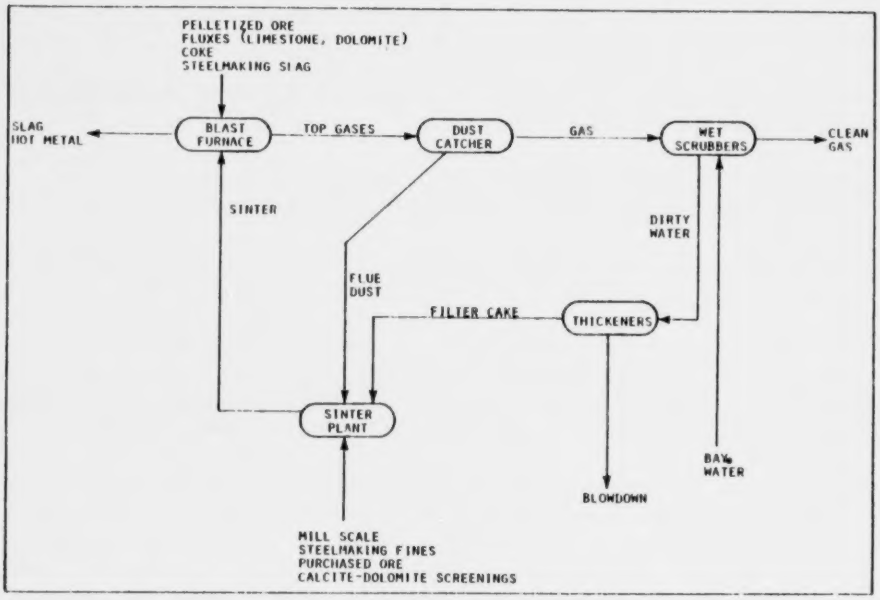
PELLETIZED ORE
FLUXES (LIMESTONE, DOLOMITE)
COKE
STEELMAKING SLAG
SLAG
HOT METAL
BLAST FURNACE
TOP GASES
DUST CATCHER
GAS
WET SCRUBBERS
CLEAN GAS
SINTER
DIRTY WATER
FLUE DUST
FILTER CAKE
THICKENERS
SINTER PLANT
BAY WATER
BLOWDOWN
MILL SCALE
STEELMAKING FINES
PURCHASED ORE
CALCITE-DOLOMITE SCREENINGS

Figure 1: Zinc Paths in the Blast Furnace/Sinter Plant System - Once-Through Water Flow

Zinc outlets from the system include the small amounts contained in the molten iron and slag tapped from the blast furnaces, and the low concentrations contained in thickener overflows returned to Hamilton Bay. The zinc concentration in this water was about 10 mg/L.

When we commissioned the recirculation systems for gas scrubber water at "B", "C" and "D" blast furnaces, zinc levels in the blast furnaces quickly rose above the critical levels. Recirculation of the washwater had to be discontinued to avoid damaging the blast furnaces. There were also other problems in the water system, where heavy, gelatinous precipitates deposited on the cooling tower, parts of which collapsed.

Figure 2 schematically represents the zinc flows in the system under recirculation conditions. The volume of thickener overflow rejected to the Bay was reduced under this mode of operation. Zinc outputs from the system were less than under once-through conditions, and as a result, zinc levels in the blast furnaces were higher at the balance point.

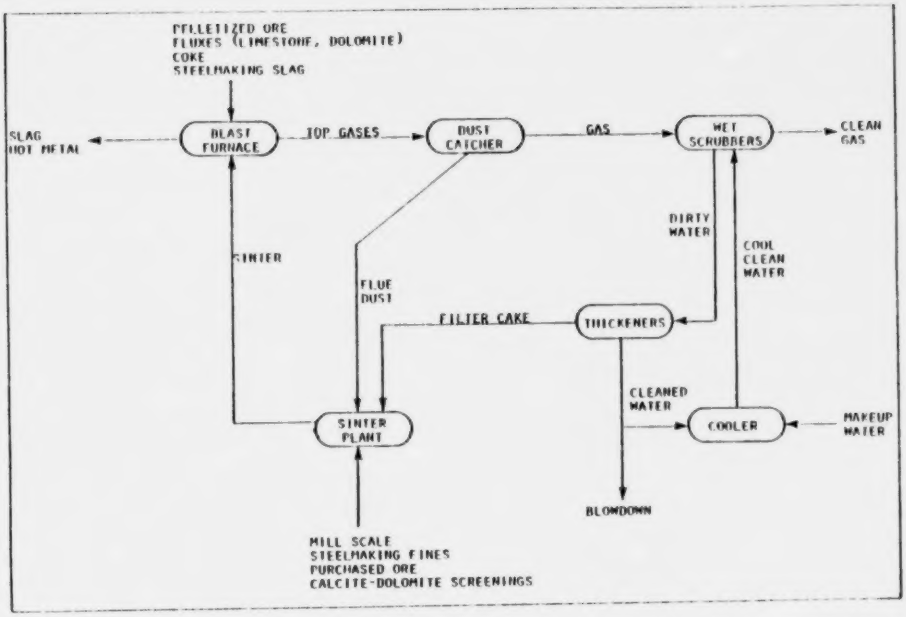
PELLETIZED ORE
FLUXES (LIMESTONE, DOLOMITE)
COKE
STEELMAKING SLAG
SLAG
HOT METAL
BLAST FURNACE
TOP GASES
DUST CATCHER
GAS
WET SCRUBBERS
CLEAN GAS
DIRTY WATER
COOL CLEAN WATER
SINTER
FLUE DUST
FILTER CAKE
THICKENERS
CLEANED WATER
COOLER
MAKEUP WATER
SINTER PLANT
BLOWDOWN
MILL SCALE
STEELMAKING FINES
PURCHASED ORE
CALCITE-DOLOMITE SCREENINGS

Figure 2: Zinc Paths in the Blast Furnace/Sinter Plant System - Recirculated Water

It was subsequently found possible to operate the blast furnaces at acceptable zinc levels under recirculation conditions provided all blast furnace dusts were dumped, at an estimated rate of about 40 000 tonne/year, rather than recycling them (figure 3). This solution to our zinc problem would replace a water environmental problem with a solid waste disposal problem - a situation not acceptable in our operations, where wastes recycling is a strong tradition. A better alternative was needed for keeping zinc at an acceptable level for blast furnace operation, while recycling as much as possible of the flue dust and filter cake. A method of bleeding zinc from from the system was necessary, which would give the same zinc-purging action as the old once-through washwater system.

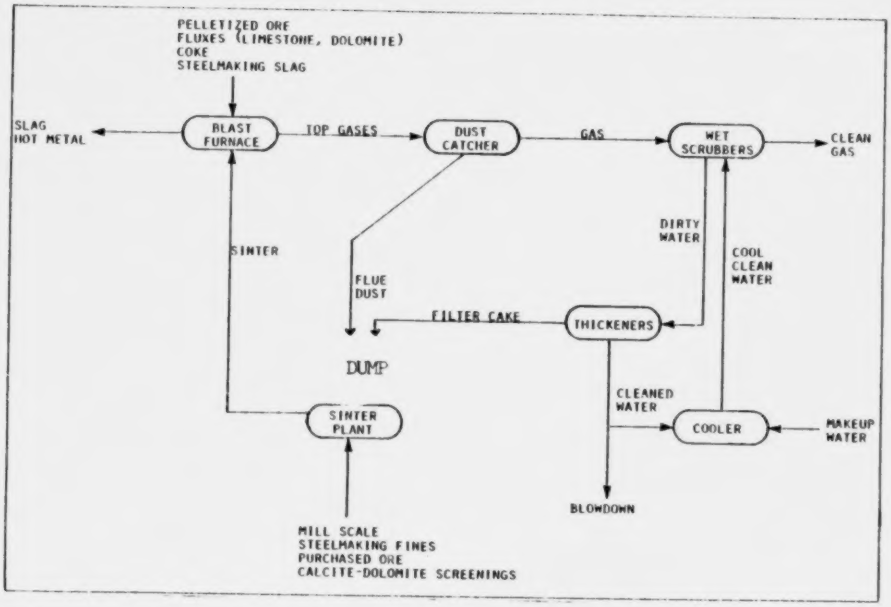
PELLETIZED ORE
FLUXES (LIMESTONE, DOLOMITE)
COKE
STEELMAKING SLAG
SLAG
HOT METAL
BLAST FURNACE
TOP GASES
DUST CATCHER
GAS
WET SCRUBBERS
CLEAN GAS
DIRTY WATER
COOL CLEAN WATER
SINTER
FLUE DUST
FILTER CAKE
THICKENERS
DUMP
CLEANED WATER
COOLER
MAKEUP WATER
SINTER PLANT
BLOWDOWN
MILL SCALE
STEELMAKING FINES
PURCHASED ORE
CALCITE-DOLOMITE SCREENINGS

Figure 3: Zinc Paths in the Blast Furnace/Sinter Plant System - Recirculated Water, Dumped Blast Furnace Dusts

METHODS OF ZINC PURGING

A state-of-the-art review revealed that, although the conventional practices of rejecting zinc in water effluent or in solid wastes are no longer environmentally satisfactory, most steel companies in the world still practice one of these two disposal methods. Nevertheless, the state-of-the-art review suggested that there might be several other possibilities.

REDUCTION PROCESSES

A few companies in Japan and Germany treat the contaminated wastes in a separate kiln process to remove the zinc. The non-ferrous metals are collected as a flue dust by-product, while the purified iron oxides, reduced to sponge iron in the process, are usable in blast furnace or steelmaking, since they are freed of zinc contamination.

This route is expensive, in both capital and operating costs. One plant manufacturer estimates (optimistically) that the economic break-even size for a plant is 400 000 tonne/yr (about ten times the amount of blast furnace dusts normally recycled by Stelco in a year). In Germany and Japan, there are examples of centralized processing facilities serving several companies, which by processing other zinc-contaminated wastes (eg steelmaking dusts) as well, achieve economic operation. One Japanese steel company recently closed down its waste-processing kiln because the process was too costly.

Several reduction processes have been mooted for application in North America, but none have reached the stage of full-scale commercial exploitation for zinc removal from steel plant wastes, primarily for economic reasons.

Processes which are feasible in principle include the SL/RN process, developed for iron ore reduction; the Wälz process for the processing of zinc-containing wastes; the Kowa-Seiko process of chloride reduction-roasting for zinc recovery; and the Inmetco process, used for the recovery of electric furnace waste oxides.

LEACHING

Substantial amounts of zinc contamination can be dissolved from iron oxide wastes with acid or alkali. If sufficient purification were achievable, the leached oxides could be recycled through a sinter plant. However, a zinc-rich residue would still require disposal.

Such processes have been widely studied in the laboratory. Several processes have been patented and pilot plants are known to have operated in the United Kingdom, Luxembourg and Sweden. None have become commercial yet because of a combination of operating and economic problems. Our laboratory studies of the leaching concept indicate that only about half the zinc in steelplant iron oxide wastes is readily removed by acid or alkali - a severe technical limitation.

PHYSICAL METHODS

Zinc tends to be associated more strongly with the smaller particles in blast furnace dusts. Separation of the smaller particles is therefore a way of preparing a zinc-rich fraction of the waste.

The principle of the method was worked out in France[1] and in Japan[2]. Separation systems based on rejecting the zinc-rich, fine particles in a wet system have been reported operating in Czechoslovakia[3] and Japan[4]. The rejected zinc-rich fraction can be processed to recover the zinc if commercial facilities are available[4] or else it can be dumped. In either case, the volume of residue is a fraction - perhaps one-quarter - of the unprocessed waste which would otherwise have to be rejected.

PRECIPITATION FROM WATER

In principle, substantial amounts of zinc can be removed from the water circuits by a combination of precipitation and settling. For example, water-softening techniques might be contrived to remove dissolved zinc from the water along with other undesirable contaminants.

Our test work indicated such techniques were feasible in principle. Zinc-rich suspended matter and precipitated zinc hydroxide were successfully removed in a small reactor clarifier.

ZINC PURGING CONCEPT

Experimental studies of all the alternatives listed in the previous section showed each had some potential for solving our zinc problem. We focused attention on choosing a method which could be incorporated into our existing operations with minimum equipment and process changes.

The chosen strategy was to purge zinc from a point in the blast furnace/sinter plant system, so that zinc concentration in the blast furnace dusts remained low enough for direct recycling to the sinter plant. Measurements indicated that, under our conditions, we would probably need to purge about 20 to 40 kg/h of zinc from the system to maintain acceptable furnace operations at low blowdown rates. However, this data was indeterminate and the first concern was to obtain a reliable estimate of this important design parameter.

There were many possible locations in the system from which zinc might be purged. The combined water-washing circits of the blast furnaces at Hilton Works form a highly complex network containing several miles of piping. Comprehensive analysis of the various process streams revealed that a recirculation stream - designated the "Return Pit Flow" - was enriched in zinc. This stream was diverted from the system to a treatment lagoon for a test period of 10 weeks, thus purging zinc continuously, as shown in figure 4.

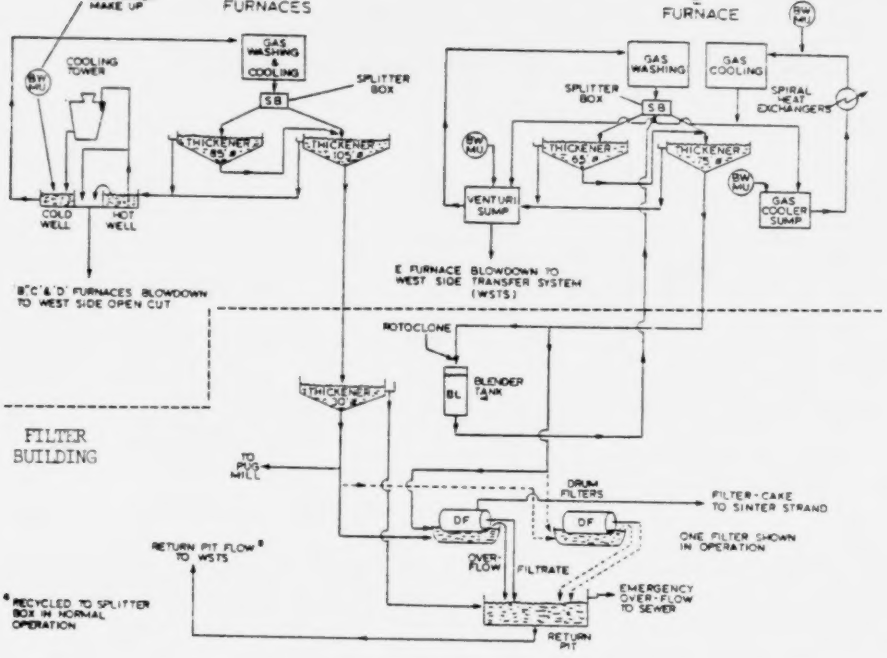
BAY WATER MAKE UP
'B' 'C' & 'D' FURNACES
COOLING TOWER
BW MU
GAS WASHING & COOLING
SPLITTER BOX
SB
THICKENER 85' ⌀
THICKENER 105' ⌀
COLD WELL
HOT WELL
'B' 'C' & 'D' FURNACES BLOWDOWN TO WEST SIDE OPEN CUT
'E' FURNACE
BW MU
GAS WASHING
GAS COOLING
SPLITTER BOX
SB
SPIRAL HEAT EXCHANGERS
BW MU
THICKENER 65' ⌀
THICKENER 75' ⌀
BW MU
VENTURI SUMP
GAS COOLER SUMP
E FURNACE BLOWDOWN TO WEST SIDE TRANSFER SYSTEM (WSTS)
ROTOCLONE
BL
BLENDER TANK
THICKENER 30' ⌀
FILTER BUILDING
TO PUG MILL
DRUM FILTERS
DF
DF
FILTER-CAKE TO SINTER STRAND
ONE FILTER SHOWN IN OPERATION
RETURN PIT FLOW* TO WSTS
OVER-FLOW
FILTRATE
EMERGENCY OVER-FLOW TO SEWER
RETURN PIT
* RECYCLED TO SPLITTER BOX IN NORMAL OPERATION

Figure 4: Flow Diagram - BCD and 'E' Furnace Recirculation System - Slurry Recovery System - Arrangement during Return Pit Trial

SUCCESSFUL OPERATION AT LOW BLOW-DOWN

The continuous purge of zinc enabled the water-recirculation system to be successfully operated at low blowdown rates while recycling all flue-dust and filter-cake to the sinter plant. In previous attempts to operate under these conditions, without a zinc purge, zinc levels in the blast furnace began to approach dangerous levels after only a few days of operation at a blowdown rate of 30 percent of the total flow. Using a zinc purge rate averaging 27 kg/h, we were able to operate at successively lower blowdown rates, while keeping zinc levels well within the acceptable range for blast furnace operation (figure 5). Ultimately, the system operated at the lowest blowdown rate achievable hydraulically (13 to 16 percent) for a period of 30 days.

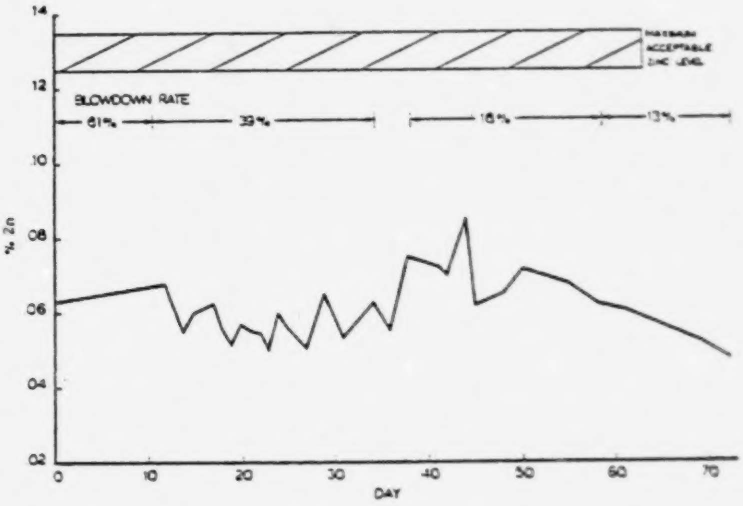

Figure 5: Zinc Content of Sinter

Water stability conditions in the recirculation system were easily controllable. No deposition, scaling or corrosion problems arose during the trial period, even though dissolved solids content of the water rose by a factor of four.

DETAILS OF THE PURGE METHOD

The Return Pit Flow, diverted from the system to a treatment lagoon, comprised contributions from three sources.

1. Filtrate from the sludge drum-filters,
2. Overflow from a small thickener in the Filter Building, fed with thickener sludge,
3. Intermittent overflow from the sludge drum-filters.

Separating these contributing flows for trial purposes was not possible without complex engineering work, so we simply diverted the whole of the Return Pit Flow, recognizing this method might not be the most desirable way to get the maximum zinc purging effect.

The Return Pit Flow was purged at about 2000 L/min for ten weeks, before cold-weather effects on equipment and detrimental effects on the behaviour of the treatment lagoon forced the trial to be terminated. The ten-week trial ended with a 30-day period at the lowest blow-down rates achievable hydraulically.

The amount of zinc purged from the system via the Return Pit Flow fluctuated widely from day to day, but there was no apparent upward trend as blowdown rate was reduced (figure 6).

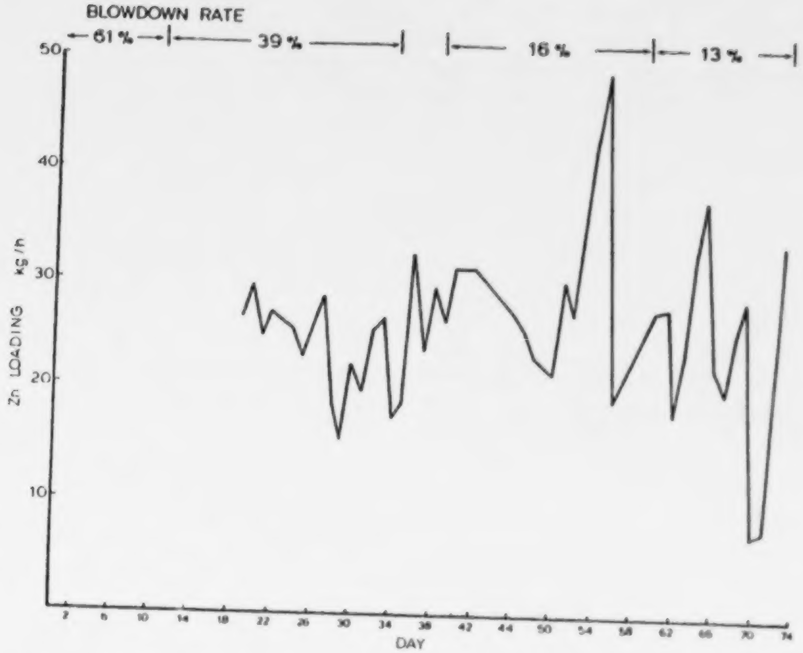

Figure 6: Zinc Loading at Return Pit

These wide swings are an operating characteristic of our system. Periodic flushing of zinc via the top gases is typical of blast furnace operation. Fluctuations in suspended solids concentrations also arise from our slurry handling practice.

FUTURE PLANS

The next stage in the development is the design and construction of a permanent zinc-purging system. The system will use the principle of separating a zinc-containing stream. The stream finally selected will depend on several economic and technical factors.

An obvious candidate is the Return Pit Flow diverted during the trial, over 80 percent of which is overflow from the Filter Building thickener. Table I shows that this thickener acts as a particle size classifier, which results in zinc enrichment of the overflow solids. This characteristic is an attractive feature, since discarding a zinc-enriched stream will require disposal of smaller amounts of solid waste. An economic assessment of capital and operating costs of several alternatives is being made.

TABLE I: ZINC CONTENT AND SIEVE ANALYSIS OF SOLIDS IN THE FILTER-BUILDING THICKENER

Process Stream	Content Zinc of Solids %	Sieve Analysis* of Solids	
		+45 µm Fraction %	-45 µm Fraction %
Inflow	3.4	32	68
Overflow	4.8	11	89

* portion retained on, or passing through No 325 sieve

So far as we are aware, a thickener has not been used as a zinc-enrichment device previously. In Japan[4], a hydrocyclone has been used to achieve zinc enrichment in a similar way to that achieved in our existing Filter Building thickener. In Czechoslovakia[3], the fine particle fraction collected by a venturi washer in the gas-cleaning system was treated separately from the coarser dust collected in a wet scrubber. The fine particle fraction was directed to a separate thickener and discarded.

Using the Return Pit Flow as the the zinc purging stream will still present disposal problems, as our experience indicates it has deleterious effects when fed directly to a treatment lagoon and filtration plant. Clarification will be necessary to remove the suspended solids. These zinc-contaminated wastes still present disposal problems, but at least the amount to be disposed of has been reduced to about 10 000 tonne/year. The filtrate is of similar composition to water blowdown from the recirculation system and we envisage it will be given the same treatment.

CONCLUDING REMARKS

We have some way to go, then, before we bring into permanent operation a satisfactory system for zinc control. In this connection, it is worth noting that generally in the steel industry, it takes about 15 years to introduce a major process change from the time of initial development to full-scale application in the developing company. It looks as if development of a satisfactory blast furnace water recirculation and zinc control system will fit into a similar time scale.

This symposium's stated purpose of providing a forum for the exchange of information on technology problems related to environmental control encouraged us to present this paper at a stage when a solution to our zinc control problem is still incomplete. Our task is a good illustration of the depth and complexity of the technical problems often faced by industry in conforming to the environmental demands placed on it.

The problem of adequate zinc control in blast furnaces with a recycled waste load is a complex situation. In this paper, we have demonstrated that a requirement to reduce volumes and levels of contamination of water discharges is not easily met, even though it may appear simple and straightforward to an unitiated outsider. Such a requirement has wide ramifications on the operation of the steelplant, with difficulties which were not at first recognized either by the environmental authorities or by the steelplant operators.

The topic of zinc control in blast furnaces is also an example of the growing conflict between requirements for air and water quality control and reduction in the volume of solid wastes. Too often, improvements in the quality of air and water discharges are demanded which result, unthinkingly, in increased generation of solid wastes. The interaction between these conflicting environmental factors needs to be examined to see whether worthwhile trade-offs can be made and to decide what developments are needed to dispose of satisfactorily the increasing amounts of solid residues from air and water quality control activities.

We hope this paper has directed your thoughts to the importance of these topics.

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2. H. Toda et al, "Separation of Nonferrous Metals from Blast Furnace Flue Dust by Hydrocyclone", Nippon Steel Technical Report No 13 (1979), pp 73-79.

3. J. Vesely, "Method of partial separation of zinc from blast furnace flue dust", Hutn. Listy, 1979, 34 (12), pp 876-77.

4. S. Uno et al, "Dezincing Equipment and Operation Based on Wet Classification of Wet Cleaned BF Dust", Nippon Steel Technical Report No 13 (1979), pp 80-85.

INVESTIGATION OF REVERSE OSMOSIS FOR THE TREATMENT OF RECYCLED BLAST-FURNACE SCRUBBER WATER*

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ABSTRACT

Entrained dust in blast-furnace off-gas must be removed before the gas can be used as fuel. Wet scrubbing is the standard method for cleaning blast-furnace gas. Scrubber water, in addition to removing dust, also dissolves contaminants including ammonia, phenol, and cyanide from the blast-furnace gas. The scrubber water is contained in a recycle system and a sidestream must be discharged to prevent scaling in the recycle system.

The objective of this research was to evaluate reverse osmosis (RO) as a candidate technique to minimize the quantity of wastewater discharged from the gas-scrubber recycle system. The RO permeate would be recovered as make-up water for the recycle system. The concentrate stream would be discharged for further treatment or possible evaporation via slag quench. Samples of blast-furnace recycle water were obtained from a local facility, and tests were conducted with a spiral-wound cellulose acetate RO module at a pH of about 5. Operating pressures investigated ranged from 350 to 450 pounds per square inch, gage, and feed operating temperatures were varied between 74 to 86°F. Permeate flux rates (gallons/day/square foot) were measured as a function of water-volume recovery level. Recovery levels ranged from 10 percent to over 80 percent.

Low membrane rejections were obtained for phenol, free cyanide, thiocyanate, and sulfide, indicating that these substances would be returned via the permeate to the recycle loop. Consequently, significant reductions in the discharge loadings of these materials could be achieved in the concentrate stream. There are indications that these substances may not be conserved in the recycle system and, therefore, may not increase in concentration within

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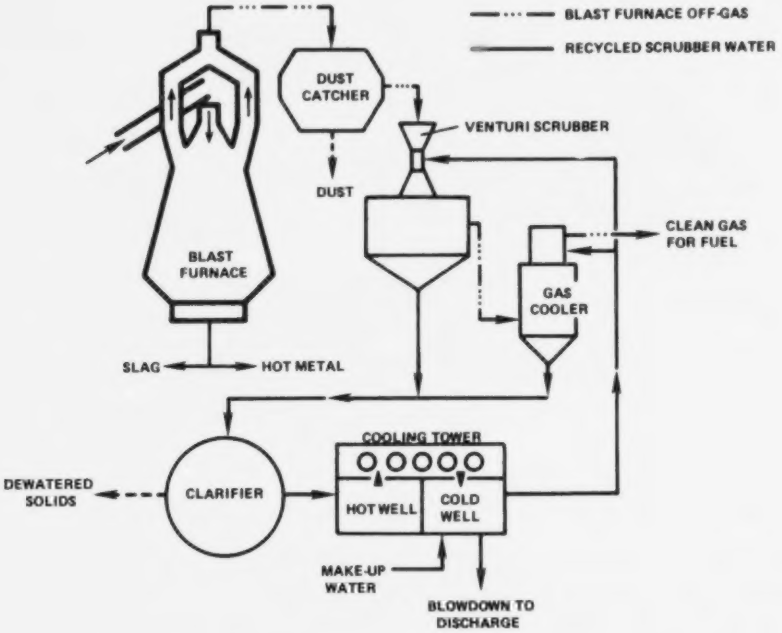
* This paper is based on an M.S. Thesis submitted by M. E. Terril in partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering at the University of Pittsburgh.

the system. Aqueous-discharge reductions of 70 percent to 80 percent appear to be possible.

Evaluation procedures for the RO system are discussed, applicability advantages and disadvantages are reviewed, and conceptual flow diagrams showing further treatment and disposal options for the reject stream are presented.

INTRODUCTION

Entrained dust in blast-furnace off-gas must be removed before the gas can be used as fuel. Wet scrubbing is the standard method for cleaning blast-furnace gas. As illustrated in Figure 1 the scrubber water is contained in a recycle system. A sidestream (blowdown) is discharged to prevent scaling or corrosion in the recycle system.



BLAST FURNACE OFF-GAS
RECYCLED SCRUBBER WATER
DUST CATCHER
VENTURI SCRUBBER
DUST
CLEAN GAS FOR FUEL
BLAST FURNACE
GAS COOLER
SLAG
HOT METAL
COOLING TOWER
DEWATERED SOLIDS
CLARIFIER
HOT WELL
COLD WELL
MAKE-UP WATER
BLOWDOWN TO DISCHARGE

Figure 1. BLAST-FURNACE GAS SCRUBBER RECYCLED WATER SYSTEM

Presently, wastewater discharged from the gas-scrubber recycle system is subject to Best Practical Control Technology Currently Available (BPT) limitations. Compliance with Best Available Technology Economically Achievable (BAT) and Best Available Conventional Control Technology (BCT) limits will be required by July 1984. These limits have been proposed by the U. S. Environmental Protection Agency (EPA) and are shown in Table I. Additional treatment will be required to achieve BAT limits. Alkaline chlorination is, currently, the treatment method recommended by the EPA. For those systems that have blast-furnace-slag quenching facilities, the gas-scrubber recycle-system blowdown may be disposed of by evaporation on hot slag. Prior research was conducted by Osantowski and Geinopolos[1)] who investigated ozonation, alkaline chlorination, and reverse osmosis (RO) with polyamide membranes followed by alkaline chlorination or ozonation of the RO concentrate as treatment approaches for gas-scrubber blowdown water. Our study was based on the use of RO for treatment of waters discharged from cooling-water recycle systems [2,3)] and advanced the work of Osantowski and Geinopolos by investigating spiral-wound cellulose acetate membranes. The use of conventional spiral-wound cellulose acetate membrances represents significant potential capital cost savings. Figure 2 is a sketch of a typical spiral-wound membrane. A second reason for selecting cellulose acetate was that it displays low rejections of cyanide and phenol at pH values below 7.

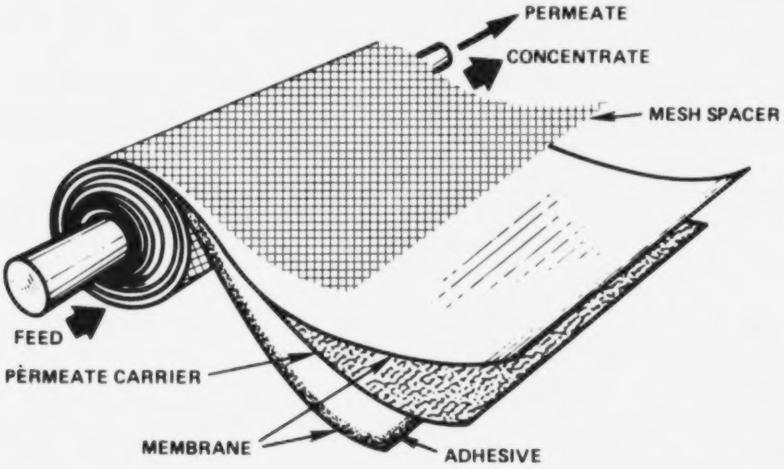
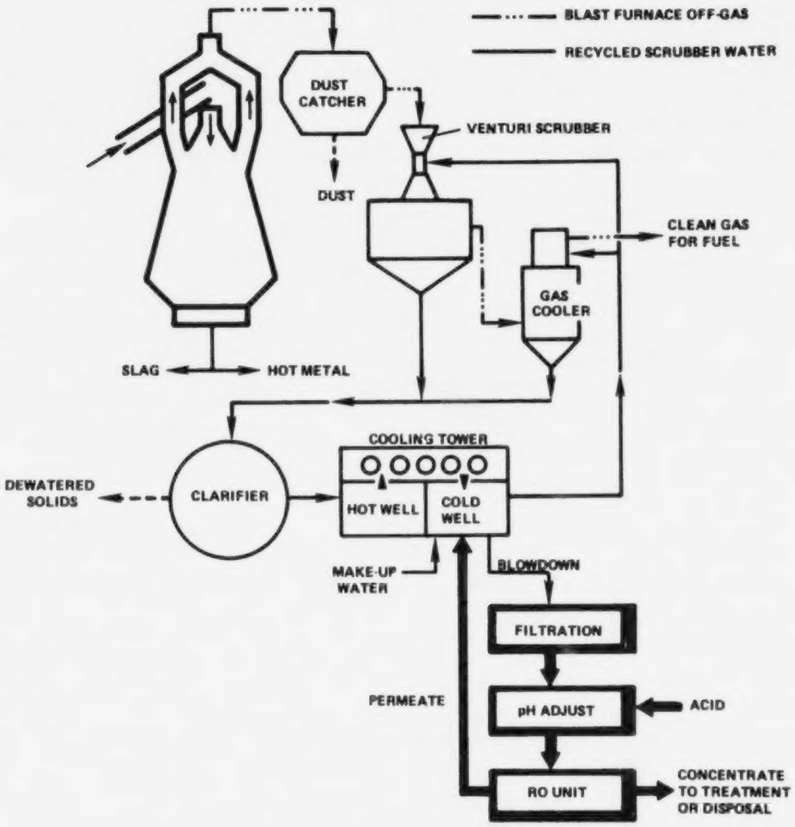


Figure 2. SPIRAL WOUND MEMBRANE CONFIGURATION

Consequently, these contaminants should enter the RO permeate, which would be recovered for reuse within the gas-scrubber recycle system. This concept is shown in Figure 3. The EPA[4)] has indicated that gas-scrubber recycle systems reduce the discharge of contaminants over a once-through system. This would indicate that some mechanism, perhaps biological, exists to limit contaminant (cyanide and phenol) loadings. Return of these contaminants to the recycle system via an RO permeate stream would be expected to cause no increase in the recycle-system loadings.

Cellulose acetate rejects calcium, magnesium, and sulfate, which are scaling components, and chloride, a corrosive component. It is expected that these substances would be removed via the concentrate stream where they are discharged.


BLAST FURNACE OFF-GAS
RECYCLED SCRUBBER WATER
DUST CATCHER
DUST
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GAS COOLER
SLAG
HOT METAL
COOLING TOWER
DEWATERED SOLIDS
CLARIFIER
HOT WELL
COLD WELL
MAKE-UP WATER
BLOWDOWN
FILTRATION
PERMEATE
pH ADJUST
ACID
RO UNIT
CONCENTRATE TO TREATMENT OR DISPOSAL

Figure 3. REVERSE OSMOSIS TREATMENT OF RECYCLED SCRUBBER WATER BLOWDOWN

Table 2 is a partial listing of the contaminants found in the blast-furnance gas-scrubber recycle-system water used in this study.

EXPERIMENTAL METHOD

The test device utilized in this research was an OSMO-1960-SS97PES pilot scale unit manufactured by Osmonics Inc. It is rated for a permeate flow of 12.4 gallons per hour (gph) and a concentrate flow of 87.2 gph at a 600 pounds per square inch, gage (psig) operating pressure with Osmonics SEPA-97 membrane. This membrane was used in the evaluation and its characteristics are detailed in Table 3.

Scrubber water samples (55 gallons each) were obtained from a local blast-furnace facility. The pH was adjusted to 5.0 ±0.2 units with sulfuric acid prior to testing to destroy alkalinity, and to shift the dissociation equilibrium for cyanide and phenol to their unionized state. Operating pressures investigated ranged from 350 to 450 psig, and feed temperatures were varied between 74 to 86°F. Permeate flux rates (gallons per day per square foot, gpd/ft^2) were measured as a function of water-volume recovery level. A flow diagram of the experimental set-up is shown in Figure 4. Recovery levels ranged from 10 percent to approximately 80 percent. Two control runs with distilled water were made before each experimental run. The first control was run at an operating pressure of 400 psig and a feed temperature of 74°F to detect changes in membrane performance. The second control was run at the experimental conditions to determine the scrubber-water osmotic pressure. A series of six tests was conducted to determine membrane rejection values of the contaminants listed in Table 1. All the test work was conducted in a batch mode. Data were analyzed according to the solution-diffusion model describing RO water and solute transport[5,6] as outlined below.

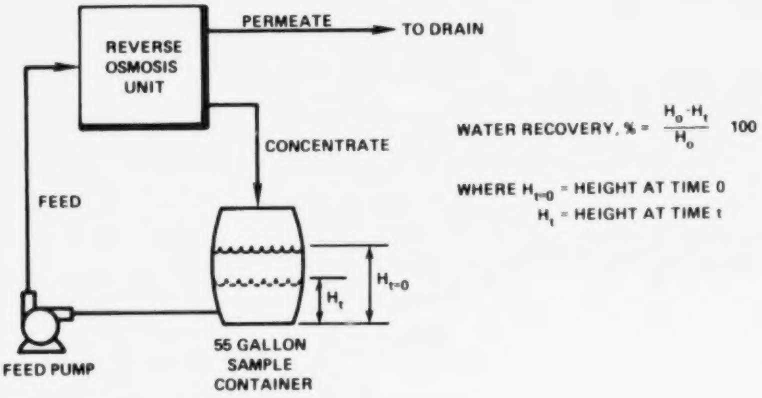
REVERSE OSMOSIS UNIT
PERMEATE
TO DRAIN
CONCENTRATE
FEED
FEED PUMP
55 GALLON SAMPLE CONTAINER
H_t
$H_{t=0}$
WATER RECOVERY, % = $\frac{H_o - H_t}{H_o}$ 100
WHERE $H_{t=0}$ = HEIGHT AT TIME 0
H_t = HEIGHT AT TIME t

Figure 4. EXPERIMENTAL SET-UP FOR WATER RECOVERY TESTING

EXPERIMENTAL AND THEORETICAL APPROACH AND RESULTS

WATER TRANSPORT

Membrane water flux rate is a function of the effective pressure applied across the membrane described by the following equation:

$$F_w = W_p\,(\Delta P - \Delta\pi) \qquad (1)$$

where

F_w = membrane water flux rate, gpd/ft^2

W_p = water permeability coefficient, gpd/ft^2/psig

ΔP = differential applied pressure across membrane, psig

$\Delta\pi$ = differential osmotic pressure across membrane, psig

Membrane water flux rates declined with increasing water recovery levels due to increasing solution osmotic pressure caused by membrane solute rejection. Observed flux declines with water recovery are presented in Figures 5 and 6. Operating pressures were varied at 350, 400, and 450 psig levels with feedwater temperatures ranging from 74°F to 86°F.

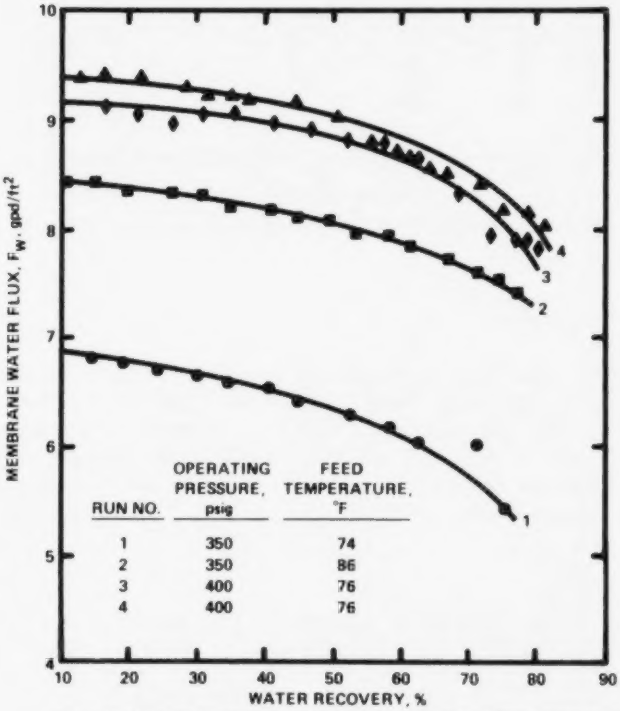

Figure 5. MEMBRANE WATER FLUX DECLINE WITH WATER RECOVERY

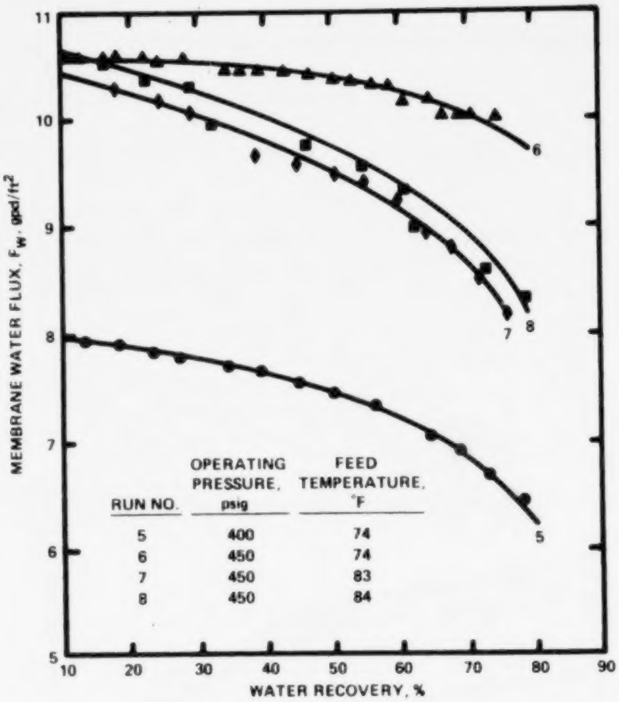

Figure 6. MEMBRANE WATER FLUX DECLINE WITH WATER RECOVERY

Water flux rates are also influenced by temperature because of the dependence of the water permeability coefficient on this parameter. Water permeability coefficients for the scrubber-water samples were determined by plotting water flux rates against effective applied pressure in accordance with Equation (1). These results are shown in Figure 7. Water permeability coefficient values determined in this manner are listed in Table 4.

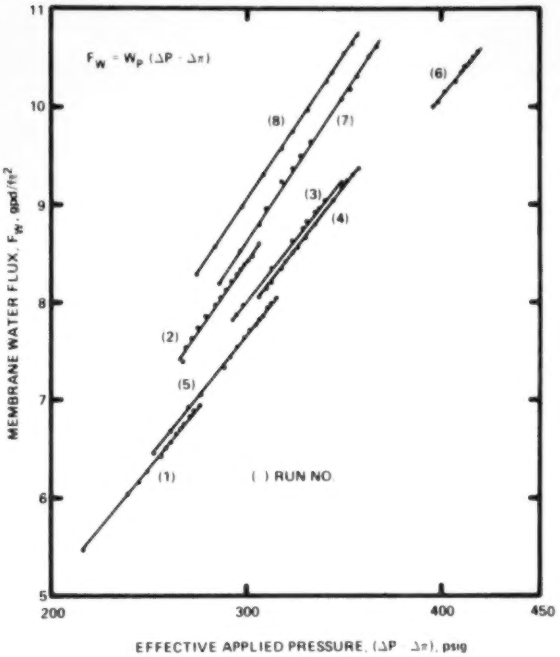

Figure 7. DETERMINATION OF THE WATER PERMEABILITY COEFFICIENT, W_p

Good agreement was obtained between values of each control run at 400 psig and 74°F, indicating no significant decline in membrane water flux rates over the test period. Agreement was also obtained between values of the control run at experimental conditions and the experimental runs. This indicates that differences observed between each of the experimental runs were due to temperature effects and not to differences in the individual samples. This temperature dependence is displayed in Figure 8. Using linear regression, the magnitude of the water permeability coefficient temperature dependence was determined as 5.4×10^{-4} gpd/ft^2.°K for the control runs at the experimental conditions, and 6.2×10^{-4} gpd/ft^2.°K for the gas-scrubber water samples. These values agree within experimental error.

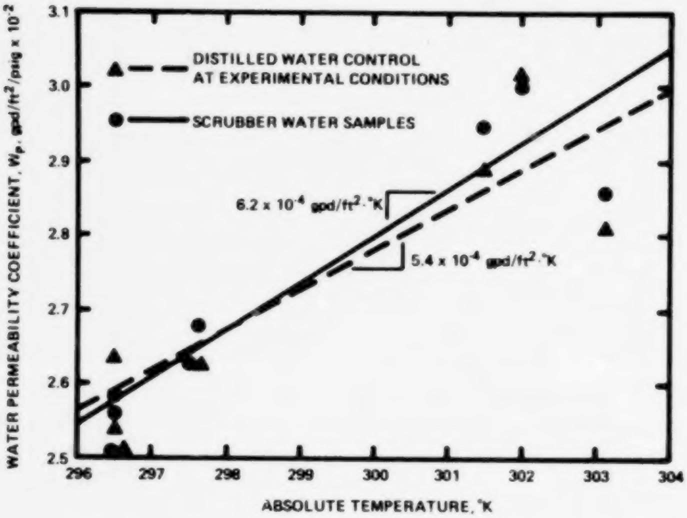

Figure 8. TEMPERATURE DEPENDENCE OF THE WATER PERMEABILITY COEFFICIENT, W_p

Water flux rates for a model full-scale RO unit were estimated by determining median flux rates from each of the flux decline runs. These rates were corrected for the observed temperature range (60°F to 90°F) of the gas-scrubber recycle system using the relationship derived above and are presented in Table 5.

SOLUTE TRANSPORT

Membrane solute flux rate is a function of the solute concentration differential across the membrane as shown by the following equation:

$$F_i = k_p (C_c - C_p) \tag{2}$$

where

F_i = solute flux, g/day/ft^2

k_p = solute permeability coefficient, l/day/ft^2

C_c = concentrate solute concentration, g/l

C_p = permeate solute concentration, g/l

Total dissolved solids (TDS) measurements were made to determine solute flux rates across the membrane in accordance with Equation (2). TDS flux rates were calculated in accordance with Equation (3).

$$F_i = \frac{F_w C_p}{C_{w,p}} \qquad (3)$$

where

F_w = membrane water flux, g/day/ft^2

C_p = permeate solute concentration, mg/l

$C_{w,p}$ = permeate pure water concentration, assumed to equal 10^6 mg/l

TDS permeability coefficients were calculated by plotting TDS flux rates against the membrane concentration difference as shown in Figures 9 and 10. The permeability coefficients obtained in this manner ranged from 1.10 litres per day per square foot (l/day/ft^2) to 1.83 l/day/ft^2.

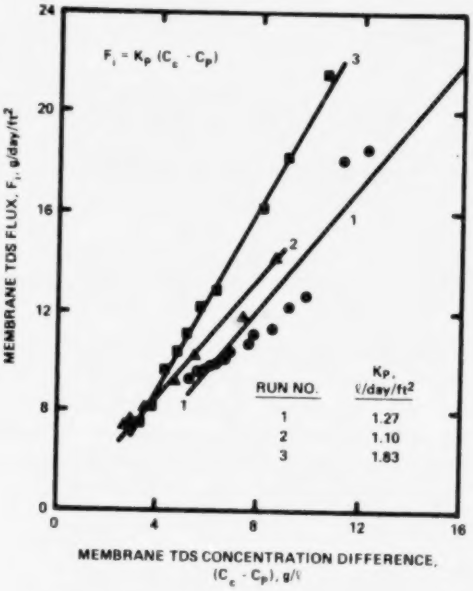

Figure 9. DETERMINATION OF THE TDS PERMEABILITY COEFFICIENT, K_p

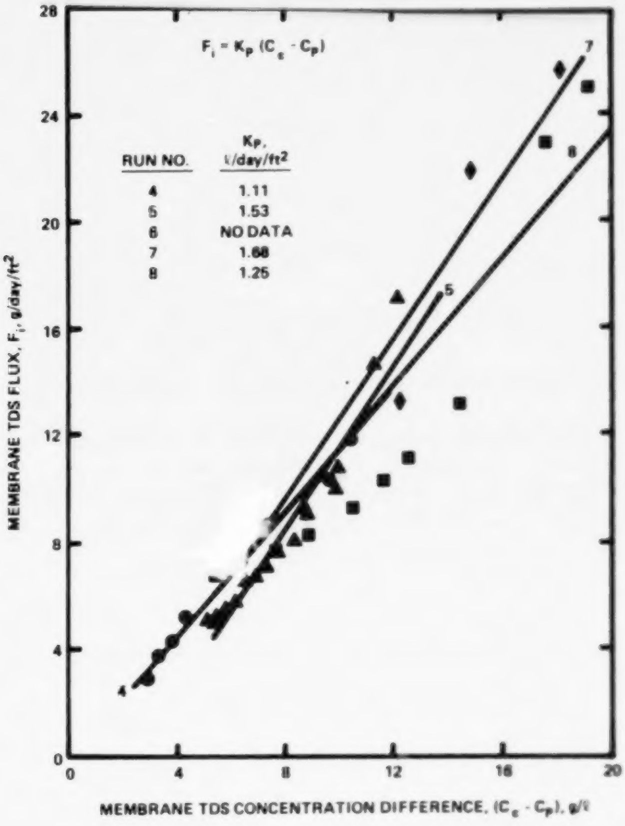

Figure 10. DETERMINATION OF THE TDS PERMEABILITY COEFFICIENT, K_p

Tests to determine rejection values for various wastewater contaminants were also conducted. These results are presented in Table 6. Negative rejections were obtained for cyanide, phenol. and sulfide, indicating preferential sorption of these materials across the membrane. Thiocyanate also displayed low rejection levels. Rejection values obtained for other contaminants examined were found to compare favorably with reported ranges in the literature.

PERMEATE WATER QUALITY

Permeate solute concentration increases directly with feed solute concentration and water recovery level. Figures 11 and 12 displays these relationships for the gas-scrubber recycle-water samples. Initial TDS concentrations of the samples ranged from approximately 2800 mg/l to 6100 mg/l resulting in permeate concentrations from 300 mg/l to 600 mg/l at a 70 percent

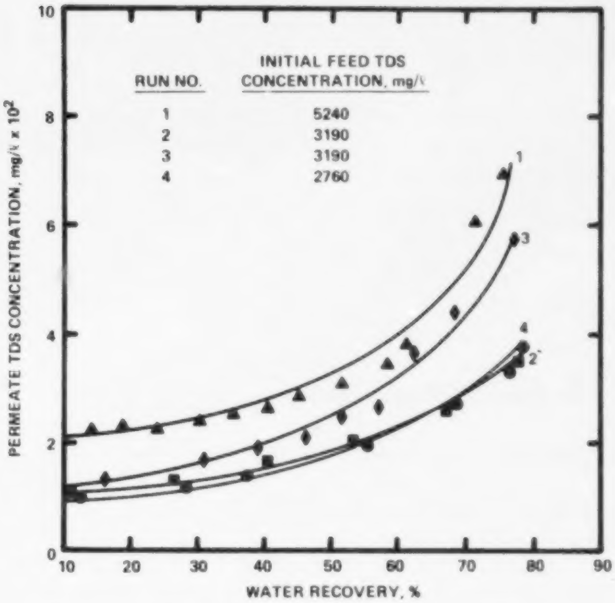

Figure 11. PERMEATE WATER QUALITY DECLINE WITH WATER RECOVERY

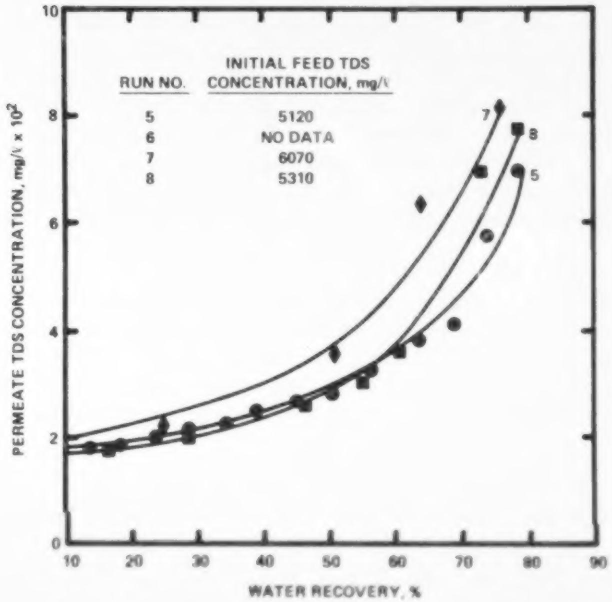

Figure 12. PERMEATE WATER QUALITY DECLINE WITH WATER RECOVERY

water-recovery level. For water-recovery levels above about 70 percent, permeate concentrations increased dramatically.

CONCENTRATION POLARIZATION AND FOULING EFFECTS

Concentration polarization is defined as the ratio of solute concentration at the membrane surface to solute concentration in the bulk solution. This may be expressed mathematically by

$$B = \frac{C_m}{C_B} \qquad (4)$$

where

B = concentration polarization

C_m = solute concentration at membrane surface

C_B = average bulk solute concentration

It is caused by concentrate solute concentration building up at the membrane surface exceeding the bulk solution concentration. When this occurs the solute tends to back-diffuse away from the membrane into the bulk solution. Concentration polarization increases the local osmotic pressure at the membrane surface, reduces membrane water flux rates, increases permeate solute concentration, and allows the concentration increase of sparingly soluble solutes, possibly causing precipitation onto the membrane. It is enhanced by high recovery levels but may be minimized by recirculation of the concentrate stream. The magnitude of concentration polarization cannot be determined directly because measurement of the membrane surface solute concentration is required. However, the presence of concentration polarization or fouling may be detected experimentally. As the solute concentration at the membrane surface increases so does the local osmotic pressure. Osmotic pressure increases more rapidly as a result of concentration polarization or fouling than would be expected simply from increases in concentrate solute concentration.

A plot of osmotic pressure versus concentrate solute concentration may be used to detect concentration polarization or fouling, as shown in Figure 13. Figure 14 is a similar plot for each of the scrubber-water samples. Linear relationships were established for each of the samples, indicating that concentration polarization and fouling effects were negligible.

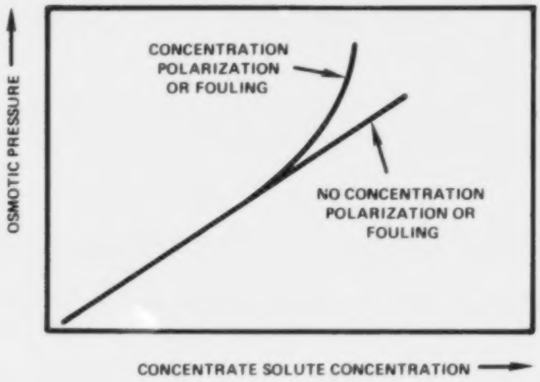
OSMOTIC PRESSURE
CONCENTRATION POLARIZATION OR FOULING
NO CONCENTRATION POLARIZATION OR FOULING
CONCENTRATE SOLUTE CONCENTRATION

Figure 13. DETECTION OF CONCENTRATION POLARIZATION OR FOULING

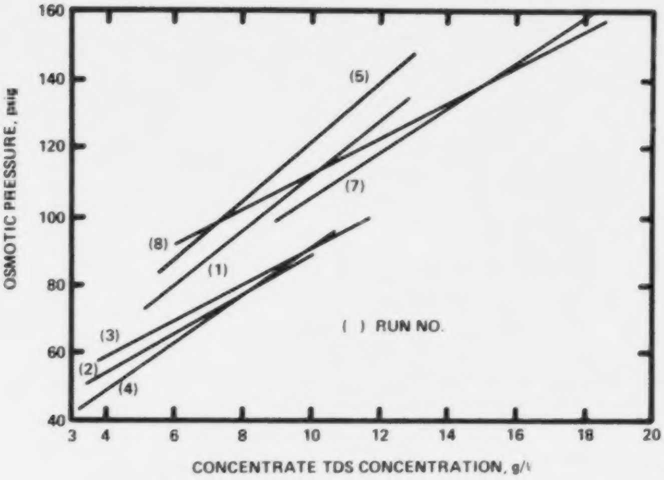

Figure 14. EVALUATION FOR THE PRESENCE OF CONCENTRATION POLARIZATION OR FOULING

APPLICATION OF RESULTS TO HYPOTHETICAL DESIGN

Calculations were prepared of the permeate and concentrate water quality from a model full-scale RO unit treating 200 gallons per minute (gpm) of gas-scrubber blowdown water. The rejection data contained in Table 6 were used instead of determining median rejection values since it was desired to obtain a conservative estimate of the contaminant loadings in the concentrate stream. These calculations are based on the average concentration values shown in Table 2.

Calculated contaminant loadings are presented in Table 7. Using conservative rejection values we find that phenol and total cyanide discharge loadings are still within proposed BAT limits while zinc and ammonia loadings exceed these limits.

Calculated reductions in contaminant discharge loadings, for a single pass through the RO unit and various water recovery levels, are presented in Table 8.

SUGGESTIONS FOR THE TREATMENT OF REVERSE OSMOSIS CONCENTRATE

Disposal of a portion of the RO concentrate may be accomplished by evaporation via quenching hot blast-furnace slag.

Treatment by alkaline chlorination and ozonation has been investigated by Osantowski and Geinopolos.[1] Both processes were found capable of achieving proposed BAT limitations and are outlined in Figure 15. Ammonia was found to

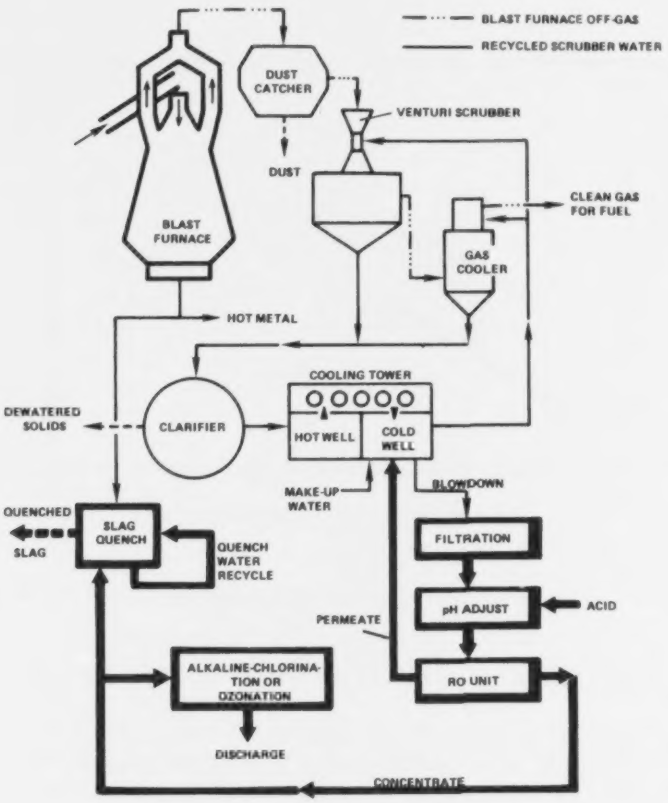
BLAST FURNACE OFF-GAS
RECYCLED SCRUBBER WATER
DUST CATCHER
DUST
VENTURI SCRUBBER
CLEAN GAS FOR FUEL
BLAST FURNACE
GAS COOLER
HOT METAL
COOLING TOWER
DEWATERED SOLIDS
CLARIFIER
HOT WELL
COLD WELL
MAKE-UP WATER
BLOWDOWN
QUENCHED SLAG
SLAG QUENCH
QUENCH WATER RECYCLE
FILTRATION
pH ADJUST
ACID
PERMEATE
RO UNIT
ALKALINE-CHLORINATION OR OZONATION
DISCHARGE
CONCENTRATE

Figure 15. TREATMENT OF REVERSE OSMOSIS CONCENTRATE

be the critical parameter for both processes such that if ammonia concentrations were reduced below BAT limits, all other oxidizable pollutants were also reduced below their respective limitations.

RESULTS AND CONCLUSIONS; SUMMARY

Based on the results of this research we may conclude that:

1. Reverse osmosis with cellulose acetate membranes appears capable of effecting significant reductions in discharge volume and contaminant loadings from a blast furnace gas-scrubber recycled-water system. Cellulose acetate membranes displayed preferential sorption of phenol (-14%), free cyanide (-3%), and sulfide (-14%) with low rejection of thiocyanate(8%).

2. Hypothetical plant calculations indicated that phenol and cyanide discharge loadings were below BAT limits.

3. High rejections of zinc (>99%) and ammonia (93%) were obtained, indicating the need for additional treatment for their removal prior to discharge. It should be noted that zinc concentrations in the samples collected were unusually high because of the composition of sinter and scrap used as blast-furnace charge. Rejections of calcium, magnesium, sulfate (>99%) and chloride (94%) were also high, assuring the reusability of the permeate stream in the recycle system.

4. Water recoveries ranging from 70 percent to 80 percent appear to be possible, although permeate water quality decreases dramatically for water recoveries exceeding 70 percent.

5. Water flux rates appeared to be adequate (5.9 to 10.4 gpd/ft^2 at 400 psig) although because of the temperature dependence of these flux rates, sizing of a full-scale unit should carefully take into account temperature variations.

6. Concentration polarization and membrane fouling did not appear to be significant. However, calcium sulfate scaling could be a major operational problem. Appropriate pre-treatment procedures, such as dispersant and anti-precipitant addition, may be required to prevent fouling of the RO membrane.

7. Studies to determine membrane permeate flux and rejection decline were not conducted because of sample limitations and the validity of performing these studies in a batch mode. These studies would have to be made in order to determine the economic feasibility of RO in this application.

8. Because of differing physical and operational characteristics of blast-furnace gas-scrubber recycle systems, additional work would be required to establish the viability of RO in this application. Recycle-water chemistry is not fully understood nor are the

operational parameters which affect it. Variabilities of contaminant concentrations would have to be determined to properly size an RO unit and to provide protection against membrane fouling.

Additional data for this study may be found in the work of Terril.9)*

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* It is understood that the information in this paper is intended for general information only and should not be used in relation to any specific application without independent examination and verification of its applicability and suitability by professionally qualified personnel. Those making use thereof assume all risk and liability arising from such use or reliance.

TABLE 1. GAS-SCRUBBER RECYCLE-SYSTEM PROPOSED DISCHARGE LIMITATIONS

lb/1000 lb IRON PRODUCED (mg/ℓ)*

	BPT	BAT	BCT
Total Suspended Solids	0.026 (50)	-	0.00438 (15)
Cyanide (Total)	0.0078 (15)	0.000292 (1)	-
Phenol	0.0021 (4)	0.0000292 (0.1)	-
Ammonia As Nitrogen	0.0535 (103)	0.000292 (1)	-
Oil & Grease	-	-	0.00292 (10 max)
Zinc	-	0.0000876 (0.3)	-
Lead	-	0.0000730 (0.25)	-

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* Concentration calculated based on 125 gallons per ton (gpt) iron produced for BPT limits, and 70 gpt iron produced for BAT and BCT limits.

TABLE 2. CONTAMINANT CHARACTERIZATION OF BLAST-FURNANCE GAS-SCRUBBER RECYCLE SYSTEM

Contaminant	Average Concentration mg/l	Standard Deviation mg/l	Maximum mg/l	Minimum mg/l	Number of Observations
Calcium as $CaCO_3$	358	76	728	190	91
Magnesium	47	10	60	34	9
Zinc	27	24	79	5	9
Conductivity umhos/cm^2	4650	1330	8200	1880	91
Total Cyanide	3.4	2.8	9.0	0.42	9
Free Cyanide	3.4	3.2	9.1	0.33	7
Thiocyanate	0.4	0.6	0.8	<0.01	2
Phenol	0.8	0.8	2.3	0.08	9
Ammonia as Nitrogen	128	31	158	55	9
Fluoride	25	6	38	19	9
Chloride	1125	278	1621	815	9
Sulfate	554	348	1265	186	7
Sulfide	0.2	0.2	0.3	<0.05	2

TABLE 3. OSMONIC SEPA-97 MEMBRANE CHARACTERISTICS

Membrane Material	Cellulose Acetate
NaCl Rejection	94-97%
Permeate Flux, gpd/ft^2 (Tap Water)	10-14@ 400 psig
Maximum Operating Pressure	800 psig
Normal Operating Pressure	400-500 psig
pH Range	2-8
Surface Area	19 ft^2

TABLE 4. WATER PERMEABILITY COEFFICIENTS, Wp, FOR CONTROL AND EXPERIMENTAL RUNS

Run Number	Distilled Water; 74°F, 400 psig (gpd/ft^2/psig)	Distilled Water, Experimental Condition (gpd/ft^2/psig)	Gas-Scrubber Water, Experimental Conditions (gpd/ft^2/psig
1	0.0251	0.0251	0.0251
2	0.0258	0.0281	0.0286
3	0.0267	0.0267	0.0268
4	0.0263	0.0263	0.0263
5	0.0255	0.0255	0.0256
6	0.0264	0.0264	0.0258
7	0.0257	0.0289	0.0295
8	0.0261	0.0301	0.0300

TABLE 5. ESTIMATED WATER FLUX RATES FOR A MODEL FULL-SCALE RO UNIT

Operating Pressure, psig	Water Flux* Rate, gpd/ft^2		
	60°F		90°F
350	5.1	-	9.0
400	5.9	-	10.4
450	6.8	-	12.6

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* Osmotic pressure of the gas-scrubber water samples ranged from 40 psig to 90 psig which is accounted for in the stated water flux ranges.

TABLE 6. OBSERVED CONTAMINANT MEMBRANE REJECTION

Solute	Average Rejection, %	Observed Rejection Range, %	Reported Rejection Range, %
Calcium As $CaCO_3$	>99	>99	96.3 to 99.7 6)***
Magnesium	>99	>99	93 to 99.9 6)
Zinc	>99	>99	
Total Dissolved Solids	97	96 to 98	89 to 99 6)
Total Cyanide*	-1	-12 to +12	-
Free Cyanide*	-3	-7 to +6	0 for pH <7 7)
Thiocyanate*	8	-10 to +24	-
Phenol	-14	-18 to -10	-20 to -10 8)
Ammonia	93	91 to 94	77 to 95 6)
Fluoride	91	89 to 92	88 to 98 6)
Chloride	94	92 to 96	86 to 97 6)
Sulfate	>99	>99	99 to 100 6)
Sulfide**	-14	-	-

* Low concentrations responsible for broad rejection range

** Only one observation was above maximum analytical sensitivity limits (0.05 mg/l)

*** See References

TABLE 7. CALCULATED DATA: APPLICATION OF RO TO BLAST-FURNACE GAS-SCRUBBER RECYCLE-SYSTEM BLOWDOWN TREATMENT

Contaminant	Permeate Contaminant Mass Flow Rate lb/day			Concentrate Contaminant Mass Flow Rate lb/day			Contaminant Mass Discharged lbs./1000 lbs. Hot Metal x 10^{-4}			BAT Limitations lbs./1000 lbs. Hot Metal x 10^{-4}
Water Recovery	70%	80%	90%	70%	80%	90%	70%	80%	90%	
Calcium As $CaCO_3$	19	33	71	841	827	789	837	824	786	-
Magnesium	2.6	4.3	9.3	110	108	103	110	108	103	-
Zinc	1.5	2.5	5.4	63	62	59	63	62	59	0.876
Total Cyanide	5.7	6.6	7.4	2.5	1.6	0.8	2.5	1.6	1.3	2.92
Free Cyanide	5.8	6.6	7.4	2.4	1.6	0.8	2.4	1.6	1.3	-
Thiocyanate	0.66	0.76	0.86	0.30	0.20	0.10	0.9	0.9	0.9	-
Phenol	1.4	1.6	1.8	0.5	0.3	0.1	0.5	0.3	0.1	2.92
Ammonia As Nitrogen	43	67	119	265	241	189	264	240	188	2.92
Fluoride	10	16	27	50	44	33	50	44	33	-
Chloride	332	523	948	2372	2181	1756	2361	2171	1748	-
Sulfate	30	51	110	1302	1281	1222	1296	1275	1216	-
Sulfide	0.3	0.4	0.4	0.2	0.1	0.1	0.2	0.1	0.1	-

TABLE 8. CALCULATED CONTAMINANT DISCHARGE LOADING REDUCTIONS, PERCENT (SINGLE PASS)

Contaminant	Water Recovery Level		
	70%	80%	90%
Calcium As $CaCO_3$	2.3	3.8	8.2
Magnesium	2.3	3.8	8.2
Zinc	2.3	3.8	8.2
Total Cyanide	70	80	90
Free Cyanide	70	80	90
Thiocyanate	69	79	90
Phenol	74	84	95
Ammonia As Nitrogen	14	22	39
Fluoride	17	27	45
Chloride	12	19	35
Sulfate	2.3	3.8	8.2
Sulfide	60	80	80

REVIEW OF WATER USAGE IN THE IRON AND STEEL INDUSTRY: BLAST FURNACE AND HOT FORMING SUBCATEGORIES

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ABSTRACT

This paper presents the results of a study of water usage and recirculation techniques in the iron and steel industry blast furnace and hot forming subcategories. The project was conducted for USEPA's Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina. Initially, a list of zero and low discharge plants in the subject subcategories was developed from information provided in the "Draft Development Document for Proposed Effluent Limitations Guidelines for the Steel Industry". USEPA wished to verify the water application and discharge rates presented in the Development Document and update this information if necessary. The work also included a determination of specific process water quality requirements in blast furnace and hot forming operations, an identification of factors which limit process water recyclability, a survey of techniques used to implement zero or low discharge systems, and a study of the feasibility of implementation of these techniques at existing plants. The study included telephone and written communications with plant personnel, American Iron and Steel Institute representatives, EPA Regional and Effluent Guidelines staff members, and equipment manufacturers, a review of technical literature, and plant visits.

INTRODUCTION

The United States Environmental Protection Agency (USEPA) had obtained information during the Effluent Guideline Development process which indicated that a number of plants in several major industrial subcategories of the iron and steel industry were operating at zero or near-zero water discharge. However, Effluent Limitation Guideline flow levels for these subcategories were set above zero discharge because the zero discharge claims had not been evaluated and substantiated by USEPA. In many cases, it was suspected that claims of zero discharge were due to inaccurate reporting or unique system operation or design.

In order to further investigate water usage in the iron and steel industry, USEPA's Industrial Environmental Research Laboratory requested Envirodyne Engineers, Inc., to conduct a project entitled "Verification and Documentation of Low Water Discharge Steel Processes". Since the available budget to fund this work was limited, the scope of work was restricted to a study of the blast furnace and hot forming categories in order to allow a thorough review. Investigation of these particular industry subcategories received high priority because of the relatively large number of plants at which these operations take place and high volumes of water utilized.

The investigation of zero and low water usage was designed to identify existing systems which are truly exemplary and which might serve as a model to improve Best Available Technology (BAT) Guidelines. Initially, information presented in the Draft Development Document for Proposed Effluent Limitations Guidelines for the Steel Industry was used to draw up a list of plants conducting blast furnace and/or hot forming operations which reported a process wastewater discharge rate less than or equal to the recommended BAT model flow rate. The Development Document recommends a BAT discharge rate of no more than 50 gallons per ton (gpt) for the Blast Furnace Subcategory. The Hot Forming Subcategory is further subdivided into primary (with and without scarfing), section (carbon and specialty steels), flat (strip and sheet, carbon plate, and specialty plate) and pipe and tube segments. Recommended BAT flow rates for hot forming operations range from 60 to 260 gpt, depending on the subcategory. The initial list of all plants with a flow less than or equal to the recommended BAT level (as indicated in the Development Document) was quite lengthy, and was shortened at the suggestion of the project officer to include only those plants which reported a discharge flow of at most 50 percent of the recommended BAT discharge rate. This list provided a numerically-manageable group of plants which had apparently achieved exemplary water use and conservation.

In order to supplement the list and identify additional plants which might be exemplary contact was made with the Cyrus W. Rice Division of NUS Corporation (which has previous experience as a contractor to USEPA in the iron and steel industry). The American Iron and Steel Institute and USEPA personnel were also contacted to identify exemplary plants and discuss water conservation techniques. These contacts allowed the study of several plants which had made improvements since the Draft Development Document was published.

In addition to contacts with individuals mentioned above, several additional approaches were utilized to verify and update water usage reported in the Development Document. Analysis of individual Section 308 responses helped clarify some of the information presented. Information published recently in technical literature updated information relative to specific plants. Telephone and written communication with representatives of each of the plants believed to be exemplary was initiated in order to confirm and update information obtained from other sources, discuss the application of treatment technologies, and inquire about the possibility of a voluntary plant visit. Direct contact with plant representatives proved to be the most useful and cost-effective means of updating information concerning individual facilities. During the course of the study, almost every plant on the original list of supposedly exemplary plants was contacted directly by phone and/or in writing.

As a culmination of the study, several plant visits were conducted. The plants selected for visits represented a wide range of sizes, ages, and status with respect to water usage. The telephone, written, and in-person visits with plant personnel provided an excellent opportunity to discuss factors which affect process water recyclability, process water quality requirements, technology useful for reduction of process water usage, and the feasibility of further reductions in water usage and discharge.

The following sections summarize results of the study and provide conclusions and recommendations to both USEPA and industry concerning rule-making and water conservation techniques.

REVISED STATUS OF WATER USAGE AT INDIVIDUAL PLANTS

In Table 1, the water usages presented in the Development Document are compared with revised water usages calculated from updated production figures and flow rates, supplied by plant representatives during the plant surveys. It can be seen that in many cases the revised figures are considerably higher than those originally reported. Several factors were found to contribute to this situation, including:

1) In some cases, there was a misinterpretation of the Section 308 Questionnaire and subsequent inaccurate responses by plant respondants.

2) Calculation of water usage in gallons per ton was based on capacity rather than actual production. With many plants operating at only 50-75 percent of capacity recently, but with no change in water application rates, calculated water use per ton of production increased accordingly.

3) Water losses through holding pond seepage or other leaks were not considered or included in water use calculations.

4) There have been changes in operations at some plants since the 308 response was submitted.

5) Several once-through systems were mistakenly representated as zero discharge.

6) In some cases represented as zero discharge, process wastes were actually cascaded to other operations and subsequently treated and discharged.

TABLE 1. UPDATED WATER DISCHARGES AND APPLICATION RATES

Plant/Code	Water Discharge Rate Presented in Development Document (gpt)	Updated Water Discharge (gpt)	Updated Water Application (gpt)
Blast Furnaces			
732A	0	4 to 28[a]	3,800
920B	?	20	1,200
856Q	0	0 (unknown amount)	4,230
860H	0	≈0	8=1,620 11=2,760 10=3,100 12=3,530
860B	?	0 (144)[b]	2,200
448A		0 (131,99)[b]	2,600 3,300
Hot Forming-Primary			
0060I	0	700	5,000
0940A	0	No information could be found	
0440A	0	0	124,000
0492A	0?	4,850[c]	4,850
684H	96	100	2,500
088D	41	11	2,100
248B	96	88[d]	5,200[d]
0060D	4	*	*
176	36	178	4,300-5,000
0612-01	78	71-120	5,900
860H-02	65	108	3,900
Hot Forming-Section			
460A	0	0[e]	12,000
672A	0	1,200	7,200
316B	0	0	13,000
396D	0	(f)	2,700
684H-01	0	42	1,040
684H-03	0	26	660
684H-06	0	190	4,700
684H-07	0	1,200	29,500
0068B	0	0	No flow data available
0060K-01	35	26	22,000
860H-03	3.5	0-104	20,800
0060I-01	0	≥1,400	6,800
0060I-02	0	≥1,700	8,300
672B-01	0	0[e]	9,400
672B-02	0	0	15,400
684H-02	0	130	3,230
088D	73	22	2,900
60F-05	59	*	*
384A-06	79	124	8,300
468B	89	168	4,800
612-01	84	{ 100-167	{ 6,600
612-04	84		
432-A	?	12,300(c)	12,300
256N	0	01=0 02=0 03=0	01=4,600 02=9,400 03=8,000
316A	0?	0	29,000
248B		88[d]	5,200[d]
Flat-Strip and Sheet			
248B	92	0	5,500
112D	0?	Unquantified Discharge	11,500
Pipe and Tube-Hot Worked			
0060R-01	0	(g)	(g)
0060R-02	0	(g)	(g)
684H	0	*	*
728	82	≈0	5,300-7,900
240B-05	0-231?	1,670	11,000
856-C	100	74	1,770

TABLE 1. UPDATED WATER DISCHARGES AND APPLICATION RATES (Continued)

NOTES:

(a) 4 gallons per ton reported by T. Oda, based on preliminary plant studies; 28 gallons per ton based on review of Data Collection Portfolios. Both values refer to discharge resulting from gas cooling and cleaning system only.

(b) Value in parenthesis is amount of evaporative blowdown off of slag.

(c) Once-through system.

(d) Average value for all alloy mills which include a blooming mill with scarfing, bar mill, merchant mill and billet mill.

(e) Suspected seepage problem.

(f) Cascading recycle system for which plant personnel could not estimate a system blowdown.

(g) These are cold worked-pipe and tube mills.

(*) A letter has been sent to plant personnel requesting updated information and no response has been received.

(?) Indicates unavailable or could not be ascertained.

7) In general, due to complicated water systems, it is usually difficult to establish exact water usage per production, and these figures are at best estimates subject to change.

The survey pointed out the relationship between site-specific production considerations and water application and discharge rates at individual plants. For example, water usage in section mills is dependent upon the desired cross-sectional area reduction of the original blooms, slabs or billets. If two mills begin with identical billets but produce products of different diameters, the mill producing the smaller diameter product would use more water per ton of steel, because more passes are required to achieve this smaller diameter. This fact may not have been fully considered in development of BAT models.

Similarly, in the production of hot formed pipe and tube, the larger the pipe diameter, the greater the water usage for direct contact cooling. If two mills start with the same raw material, a mill producing large diameter pipes would use more water per ton of product than one that produces small diameter pipes.

WATER QUALITY REQUIREMENTS

BLAST FURNACE SUBCATEGORY

Table 2 illustrates the average water quality characteristics of raw and treated process wastewater in this subcategory. This information was derived from analytical data collected during the original guidelines survey and supporting sampling and analysis program. Some typical values for these parameters in an exemplary blast furnace recycle system are also given to provide additional water quality characteristics.

As this data indicates, reduction of the suspended solids concentration is essential to the gas cleaning scrubber operation. A total suspended solids concentration of 50 milligrams per liter or less is optimal. The scrubbing of the dirty blast furnace gases results in a marked increase in the alkalinity, hardness, total dissolved solids, total suspended solids, chloride and sulfate concentrations of the process water.

HOT FORMING SUBCATEGORY

The average water quality characteristics of raw and treated process wastewater as determined from analytical data collected during the original guidelines development and supporting sampling and analysis program are presented in Table 3.

This data indicates that in the treated process wastewater of the hot forming subcategory, total suspended solids concentrations of 40 milligrams per liter or less and grease and oil concentrations of 15 milligrams per liter or less are typical. Primary, section and plate mills usually have higher grease and oil concentrations in their process waters than do hot strip mills or pipe and tube mills.

Plant representatives indicated that the following water quality requirements were important in their recycle systems:

1) Constant water quality is important if a consistently good product is to be produced.

2) Removal of water soluble oils is important because they can foul heat exchangers and cooling towers as well as inhibit the roll's ability to grip the hot metal.

3) Total suspended solids concentrations must be kept to a minimum as they can foul bearings. Larger solids can clog spray headers.

4) Some plants chemically treat to keep dissolved solids concentrations at acceptable levels.

5) Water temperatures ranging from ambient to 180°F have been used successfully.

TABLE 2. BLAST FURNACE-SUBCATEGORY WATER QUALITY REQUIREMENTS

Parameter[a]	Average Values from Original Guidelines and Toxic Pollutant Survey		Plant 448-A	
	Raw Process Wastewater	Treated Process Wastewater	Blast Furnace Make-up Water	Blast Furnace Recycle Water
pH (units)	6.4-10.2	6.7-10.9	7.3	7.1
Total suspended solids	1,038	51	39	50-300
Total dissolved solids			550	3,000
Hardness $CaCO_3$			200	900
Alkalinity $CaCO_3$				
Phenolphthalein			0	
Methyl orange			50	220
Chloride			170	1,100
Sulfates			100	370
Ammonia	72	66		
CN^-	15	9		
Phenols	1.8	1.4		
Fluoride	33	32.5		

NOTES: [a] All results in mg/l except as noted.

TABLE 3. HOT FORMING-SUBCATEGORY WATER QUALITY CHARACTERISTICS

Parameter$^{(a)}$	Primary		Section		Hot Strip and Sheet		Plate		Pipe and Tube	
	I$^{(b)}$	O$^{(b)}$	I	O	I	O	I	O	I	O
Total Suspended Solids	83	27	67.8	35	47	23.9	75	14	89	40
Oil and Grease	41	9.3	28.3	8.8	12	12	39	16	9.1	5.4

NOTES: (a) All concentrations in mg/l.

(b) I = Raw Wastewater input to treatment system
O = Effluent from treatment plant to be recycled

6) Bacterial problems have been noted and remedied by chemical addition in some closed loop systems.

7) In some plants, raw water supplies must be softened before use.

Representatives of Plant 248B, who operate a very tight recycle loop about their hot forming mills, indicated that the following water quality requirements are important.

1) Manufacturers have recommended that they operate their hot strip mill with water that has a total suspended solids concentration of 20 ppm or less, but they have successfully operated their mill with total suspended solids ranging from 30 to 200 ppm.

2) Total dissolved solids concentrations in their recycle loop have stabilized, and generally range from 700 to 900 ppm. They have experienced no fouling problems.

3) Water temperatures of less than 120°F have been specified by manufacturers but they have operated at temperatures as high as 180°F without any problems.

4) Grease and oil concentrations are kept at 5 ppm or less.

A summary of water quality requirements specified by an equipment manufacturer and by six iron and steel plants for the hot forming category is provided in Table 4. The most closely controlled operating parameters seem to be total suspended solids, total dissolved solids, grease and oil, chlorides, and sulfates. Toxic metals do not seem to present any major problems to final product quality.

TABLE 4. HOT FORMING-SUBCATEGORY WATER QUALITY REQUIREMENTS

Parameter[a]	Manufacturer Recommendations	584-F Hot Strip Run-out Table Spray	868-A Hot Forming Mills Run-out Table Spray	948-C Hot Rolling Mills Hot Strip Cooling	448-B Hot Rolling Mills	248B Hot Strip Mill Rolling Mills	German Iron & Steel Plant Hot Rolling Mills
Temperature (°F)						120-180	86
pH (units)	7.0				7.7		6.5-9.5
Total suspended solids	<25	37	25	40	50	30-200	1.0
Total dissolved solids			175	450	300	700-900	
Hardness Al_2O_3							
$CaCO_3$					120		
Alkalinity $CaCO_3$ methyl orange					70		
Grease and Oil			10	21		5	5
Chlorides	<100			61	50		
Sulfates	<300	78		143	70		
Phenol		0.015		0.03			
NH_4 (total)		0.8		3.5			
CN^-		0.037		0.11			1.0
Chromium (total)				0.04			4.0
Copper							3.0
Iron (dissolved)				0.63			
(total)				11.4			no limit
Lead				0.06			
Nickel							5.0
Zinc				0.20			5.0
Sodium		20					
BOD_5		3.0					
Nitrates		0.7					

NOTES: [a] All values in mg/l excpet as noted.

Process water temperatures vary widely from plant to plant depending on individual recycle rates per ton of hot formed product. All that is required is that the combination of water temperature and velocity be adequate to cool the rolls and in some cases the hot formed product.

FACTORS WHCH LIMIT RECYCLABILITY

This section contains a discussion of the general requirements that must be met to implement any recycle system, followed by some particular points that are specific to the blast furnace and hot forming subcategories.

GENERAL CONSIDERATIONS

Plant Layout

It is essential that process wastewaters, non-contact wastewaters, and storm water systems remain separate if high recycle ratios are to be attained. Segregation and separate treatment of incompatible waste streams also enhances recyclability.

Economics of Water Supply Versus Treatment

Depending on the source of raw water, it may be more economical to operate a once-through water system rather than treat and reuse.

Chemistry of Raw Water Supply

The blowdown necessary to avoid scaling, corrosion and fouling is dependent on the minerals present in the raw water supply.

Hydraulic Balance

The maintenance of a hydraulic balance in various portions of a closed loop system is necessary to avoid overloading the system. The system must have the capacity to handle sudden surges resulting from abnormal, necessary introductions of water to the system. If this capacity is not provided for, excessive blowdowns may be required to avoid flooding. In general, systems which are physically spread out over many acres and thereby provide for settling, cooling, and evaporation tend to reduce blowdown and maintain a high recycle rate.

Manpower Requirements

The plant must have the ability and resources (in terms of manpower) to constantly seek out and correct the sources of hydraulic leaks into the closed loop system. Otherwise, the recycle system may eventually be overloaded, resulting in the degradation of water quality or the necessity for significant blowdown.

Water Infiltration

Set procedures must be established to avoid the intentional introduction of new water into the closed loop system. For example, if an accident occurs that requires water for cooling, it should be pumped from within the system rather than utilizing fresh water. Plant workers must be fully instructed as to the proper procedures necessary for the maintenance of the closed loop.

Water Losses

If an earthen lagoon is used for solids settling, cooling or water storage, it must be properly designed to avoid possible losses which can result through seepage and/or overflow during periods of heavy rain.

Foreign Materials

The operation of the recirculation system is susceptible to the introduction of foreign materials (hardhats, cans, light bulbs, etc.). These have the potential to block flow and upset the system.

SPECIFIC CONSIDERATIONS

Blast Furnace Subcategory

The major process wastewater source in the blast furnace operation is the water used in cleaning dirty blast furnace gases. In blast furnace gas cleaning recycle systems, the following factors limit the ability of plant personnel to recycle a higher percentage of their wastewater.

Scaling is a major problem in most blast furnace gas cleaning systems. Scaling has been known to plug spray nozzles, reduce the effective area in venturi throats, and clog supply pipes. The precipitating material that causes this scaling is usually calcium carbonate. The tendency of the recycle system towards calcium carbonate scaling can be determined through the use of the Langelier Saturation Index (LSI). In the LSI system, a zero value indicates that the system is in equilibrium in regards to calcium carbonate. A positive index value indicates that there is an abundance of calcium carbonate in solution; to achieve equilibrium, the calcium carbonate will precipitate out, resulting in scaling. If the LSI is negative, there is a shortage of calcium carbonate in solution resulting in corrosion of pipes as the system tries to reach equilibrium. The contribution of calcium and alkalinity from the limestone in the flux and the carry-over of calcium chloride results in the precipitation of calcium carbonate whenever the solubility limits are exceeded in the blast furnace gas cleaning system. In many blast furnaces, the LSI is kept stable by a system blowdown and the addition of acid or anti-scaling agents.

The Ryznar Stability Index (RSI) has also been used at plants to monitor corrosion and scaling tendencies. Calculation of the RSI is based on five basic water quality parameters: alkalinity, salinity, calcium concentration, pH, and temperature. Water with an RSI value greater than six is considered corrosive, while scaling will occur when the RSI is less than six. Thus, through regular monitoring, plant operators can make periodic adjustments to the water treatment system and maintain system control.

The burden and flux materials charged to the blast furnace determine the types and concentrations of pollutants found in the dirty blast furnace gas and ultimately in the scrubber wastewater. These concentrations affect the recycle ratio.

The heat load placed upon the process water affects the recycle ratio. Evaporative cooling is often used to dissipate excess thermal energy but water is lost and pollutants concentrated. If raw water makeup is not of sufficient quality to dilute pollutant concentrations, scaling can pose a problem because dissolved solids concentrations would increase. A system blowdown must be discharged, cascaded, or evaporated from hot slag or coke in order to maintain pollutant concentrations.

Hot Forming Subcategory

In the hot forming subcategory, process wastewater results in many cases from the direct application of water to the hot formed product. Representative uses include: product and roll cooling, descaling, flume flushing, and shear spray cooling water. In primary mills, if hot scarfing is employed, a waste stream results from the hot scarfer spray flushing and cooling system and the wet gas cleaning system. Factors which limit the ability of plant personnel to recycle a higher percentage of the wastewater from hot forming operations are discussed below.

Much of the process water used in hot forming operations is applied directly to the hot formed product. If product quality requirements are to be met the recycle must be of consistently good quality. This can dictate the need for a system blowdown to keep pollutant concentrations at acceptable levels. In some hot forming finishing operations, city water must be applied to attain the required quality product.

The quality of the raw water used as make up to the system to replace water lost to evaporation, to sludge disposal, and to system blowdown, limits the amount of process wastewater the plant is able to recycle. If the raw water contains a significant concentration of calcium carbonate, the gradual accumulation of calcium carbonate due to evaporative losses unstabilizes the LSI; scaling can result. Thus, plants with better raw water quality may be able to attain a higher recycle ratio than those that do not.

Some plants indicated that suspended solids limited their ability to recycle. Spray headers used for roll cooling can tolerate particles up to about one inch in diameter before clogging. In primary mills that employ hot machine scarfers, scrubbers are required to clean the dirty combusion gases. Plugged spray nozzles and venturi throats can cause a problem if suspended solids concentrations become too great.

Normality of production also affects the recycle ratio. Highest recycle ratios are achieved when production is high and all mills are operating continuously. If the demand for steel declines, this may result in down-time for a mill; if it is for any considerable length of time, the system must be flushed to prevent clogging and corrosion of lines. The system must be blown down again before production can resume.

TECHNOLOGY USEFUL FOR REDUCTION OF WATER USAGE/DISCHARGE

BLAST FURNACE SUBCATEGORY

Wastewater generated in the blast furnace subcategory results primarily from furnace top gas cooling and cleaning. Treatment of this wastewater can consist of the following.

The initial step in the treatment of blast furnace wastewaters is the removal of suspended solids. Most plants use a thickener or similar gravity sedimentation component for suspended solids removal. Lamella thickeners work very effectively on dirty blast furnace wastewater because high incoming solids concentrations are conducive to development of a thick Lamella sludge blanket, which results in better solids removal.

The slurry from the thickener underflow is usually dewatered by vacuum filtration. The filtrate is recycled to the thickener and the sludge containing toxic pollutants and other pollutants is landfilled. In other cases, a blowdown stream is taken off the bottom of the Lamellas and evaporated off of hot slag. The water granulates the hot slag and also traps air inside it. This granulated product can be used as insulation, road bed, and even lightweight concrete if mixed with cement. Another alternative is to send the hot underflow stream in slurry form to a sinter plant. Here, the slurry would be thickened and the hot solids used as sinter strand for their iron and thermal content. The water from the slurry would be used as makeup water in the sinter plant.

To improve solids removal performance, thickeners and coagulant aids such as polymers and ferric chloride are added to the wastewater stream at the thickener inlet. These coagulant aids enhance solids removal by aiding in the formation of larger, more readily settleable particles.

A certain amount of makeup water will have to be added to the thickener/clarifier overflow before this stream is recycled to the gas cooling and cleaning system. The LSI or RSI of the recycle stream should be closely monitored and acid and descaling agents added as needed to prevent scaling.

If burden materials charged to the blast furnace result in the formation of unacceptable levels of cyanide, ammonia or phenols, alkaline chlorination may be considered. Alkaline chlorination involves addition of chlorine or sodium hypochlorite to wastewaters that have an alkaline pH. Alkaline chlorination destroys cyanides by oxidizing them to carbon dioxide and nitrogen; ammonia by oxidizing it to nitrogen and water; and phenols by oxidizing them to carbon dioxide. Care must be taken to closely monitor the input of chlorine because an excessive amount could cause chlorine cracking of metal surfaces and could result in the possible formation of chlorinated hydrocarbons.

Activated carbon may be a recommended polishing step if quantities of water are to be blown down to a municipal treatment facility. Activated carbon reduces COD, BOD, and some organic pollutant concentrations.

Open trenches may be used whenever possible to cut down on corrosion problems inherent in metal piping.

HOT FORMING SUBCATEGORY

Wastewater generated in the hot forming subcategory results primarily from roll cooling, descaling, flume flushing, shear cooling, and hot machine scarfing. As noted previously, the wastewaters generated from all hot forming operations have similar characteristics and can therefore be treated together. The following basic treatment units are generally employed: primary sedimentation, surface oil removal, secondary settling or filtration, and recycle. The following technologies are useful for reduction of water in these units.

If the scale pit is located immediately adjacent to the mill stands, the volume of flume flush water necessary to wash the scale into the pits may be reduced. Open trenches should be used as often as possible to cut down on corrosion problems. Scale pits must be easily accessible because scale must be frequently removed using heavy equipment.

Slotted tube, rope or belt-type oil skimmers are used for grease and oil removal. Grease and oil concentrations must be kept to a minimum because they can foul heat exchangers and cooling towers as well as inhibit the roll's ability to grip the hot metal.

A portion of the wastewater exiting the primary scale pit is recycled to the mill for flume flushing.

The wastewater leaving the primary scale pit is discharged to a clarifier or thickener for additional suspended solids removal. The removal of solids aids in the cooling of the wastewater. The sludge is vacuum filtered with the filtrate returned to the thickener/clarifier and the hot solids landfilled.

Many plants with the available land requirements use a settling lagoon to achieve secondary settling. This greatly enhances the cooling process but solids are not removed immediately and serve as a heat source. The disadvantages of using settling lagoons are seepage and overflow problems, which can be controlled through proper design.

Many plants use cooling towers to reduce the thermal load placed upon the roll cooling water. The wastewater must occasionally be treated with scale inhibitors and acid added to prevent scaling. Some plants must soften their raw water supply to improve recyclability.

Again, it should be stressed that separation of contact from non-contact wastewater is advantageous in achieving a low to zero discharge recycle system. By separately treating the contact wastewater the burden placed upon the treatment system is reduced. The non-contact wastewater must undergo only minimal treatment before it can be recycled.

Water application rates should be reassessed and reduced if this will not interfere with plant operation. Unnecessary water usage should be eliminated.

FEASIBILITY OF FURTHER REDUCTION OF WATER APPLICATION AND DISCHARGE RATES

The technology is available for the iron and steel industry to significantly reduce water application and discharge rates associated with blast furnace and hot forming operations. Many plants have not installed BAT technology. Lack of segregated process, non-contact, and storm water systems will severely hamper efforts to make significant improvements. In some cases, once-through systems have survived rather than being replaced by cascading water use or closed loop recirculation systems due to economic considerations. Water is often needlessly circulated through unit operations regardless of their operating status. Heated, enclosed buildings and improved management practices would eliminate this situation. The volumes of water used for direct contact cooling are often not adjusted on the basis of the water temperature. Water loss through seepage or overflow at settling/cooling ponds is a problem at some plants.

Water discharges resulting from blast furnace gas cleaning can be reduced by the methods described previously. The pollutant loads in discharges from this operation are dependent upon the burden charged to the blast furnace. Today, many plants are faced with the decision of whether to install improved water treatment technology in their existing blast furnace operation or to replace their iron making facilities with electric arc furnaces.

Evaluation of the potential for reduction of water application and discharge must be made on an individual plant-by-plant basis. Specific designs for systems cannot usually be transferred directly from one plant to another. The degree of recycle which can be economically achieved is dependent on the availability and chemical characteristics of fresh water supplies, the existing layout of the plant, and the economics of the situation. If reductions in water use and discharge to levels approaching the BAT recommended flow cannot be achieved, it is usually because of economic rather then engineering constraints. Further flow reductions to approach zero discharge will require extensive commitments from the corporation to site-specific detailed design, proper start-up, expert management, constant maintenance, laboratory support, and the education and cooperation of all plant personnel. Through these types of combined efforts, it has been demonstrated that essentially zero discharge hot forming operations can be operated over extended periods of time.

CONCLUSIONS

A review of zero and low discharge plants in the blast furnace and hot forming subcategories as selected from the Development Document for Proposed Effluent Limitations Guidelines for the Iron and Steel Industry revealed that, in many cases, the water usage/discharge reported was too low.

In the blast furnace subcategory, three of six plants reviewed had a zero discharge; all three plants accomplished this by means of an evaporative blowdown onto slag. The remaining three plants have recycle systems with discharges of less than 30 gpt of iron produced.

One of nine mills reviewed in the hot forming-primary category had a zero discharge with three other mills discharging less than the BAT recommended flow. Seven of twenty-seven mills reviewed in the hot forming-section category had zero wastewater discharge with an additional eleven mills discharging less than the BAT recommended flow. One of the two hot strip mills reviewed was a zero discharge facility. Of the six pipe and tube mills studied, only four were verified hot-worked facilities and none of these had a zero discharge. Two of these mills discharged at rates less than the BAT recommended flow.

Seven of the nine mills that have achieved zero discharge recycle systems in the hot forming subcategory are mini-mills. This achievement can be attributed to: their relative simplicity; a design that incorporates segregation of process, non-contact, and stormwater systems; the compatibility of their waste streams for treatment purposes; relatively simple treatment requirements; and the ability to maintain a hydraulic balance.

Some key elements that must be present before a zero or low discharge system is attainable are: segregation of contact, non-contact and storm water systems; proper design and operation of a hydraulically balanced system; sufficient manpower to locate and eliminate sources of water infiltration or loss; and control of water chemistry to eliminate scaling, corrosion, fouling and foaming.

In the blast furnace subcategory, reduction of the total suspended solids concentration in the gas cleaning wastewater is essential if a low to zero discharge recycle system is to be attained. Other parameters which must be controlled include alkalinity, hardness, total dissolved solids, chloride and sulfate concentrations. Scaling is a major problem in most blast furnace gas cleaning systems. Scaling has been known to plug spray nozzles, reduce the effective area in venturi throats, and clog supply pipes. The precipitating material that causes this scaling is usually calcium carbonate. Proper control of the Langelier Saturation Index (LSI) or Ryznar Stability Index by addition of acid or anti-scaling agents and an adequate system blowdown can reduce the chances of scaling. BAT Model No. 3 - 100 percent recycle - appears impractical because dissolved solids concentrations and calcium carbonate concentrations would increase. Some sort of blowdown is necessary.

whether it be an evaporative blowdown off of slag or a cascade to a sinter plant, to stabilize the LSI.

The types and quantities of pollutants found in the gas cleaning wastewater are dependent upon the burden and flux materials charged to the blast furnace, furnace operating conditions, and raw water characteristics. The technology is available to implement a very tight recycle system, but individual plant conditions will determine whether a low discharge recycle loop is economically achievable.

Wastewater characterization of hot forming-primary, section, pipe and tube, and flat mills indicates that their wastewater is similar and can be treated together. Key parameters to be controlled in hot forming wastewaters before a zero to low discharge recycle system can be implemented are total suspended solids, total dissolved solids, grease and oil concentrations, and temperature. Operating experience at individual plants indicates that water quality requirements with respect to these parameters are not particularly stringent. The technology is available to control these parameters, but achievement of a zero to low discharge recycle loop will vary from plant to plant depending on current plant layout, operating conditions, raw water characteristics, and economic considerations.

RECOMMENDATIONS

It is recommended that the revised water discharge rates obtained during this study be considered before any changes are made in regulations.

The results of this study suggest the need for an update of the status of other industry subcategories. Regularly scheduled updates in the form of annual DCP supplements would be useful to assist the USEPA in maintaining an accuate data base.

Direct financial incentives to the plants may provide the motivation to make the in-plant changes needed in water use and recirculation. These incentives might take the form of tax credits, fines or other penalities, or demonstration grants. Without these incentives, some plant operators appear complacement about maintaining a "status quo."

The economic impacts of segregation of process, non-contact, and storm water systems, and treatment of fresh water supplies to remove hardness, are highly plant-specific. In some cases, these economic impacts would prohibit the installation or improvement of water recirculation systems. Economics should therefore be considered if revisions to standards are contemplated.

In some cases, the size and shape of raw materials and intermediate or finished products affect water application rates as expressed in gallons per tons. These factors should be considered in development of standards.

Development of the technology to adjust flows based on mill throughput should be investigated. Plant operators should stop the application of water during non-productive periods whenever possible.

Plants should experiment with water quality parameters in order to identify plant-specific minimum requirements. Many plants impose unnecessarily stringent constraints for total suspended solids, grease and oil, dissolved solids, temperature, and flow. If greater toleration for these parameters is proven, on a site-specific basis, to have no adverse impact on operations and product quality, significant expenses associated with operation of recirculation systems may be eliminated.

Based on the relatively high amount of recirculation achieved by minimills, the USEPA may wish to consider separate subcategorization and regulation of this segment of the industry.

CONTROL OF SCALE FORMATION IN STEELPLANT WATER RECYCLE SYSTEMS

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ABSTRACT

Several options for scale formation control are discussed with particular reference to the recycling of scrubber water for blast furnace top gas. Experiments on carbonate scale formation are described and several important operating variables are discussed. Several types of sensors that might be used to aid in the avoidance of scaling are reviewed.

INTRODUCTION

The concentration of dissolved solids in industrial waters tends to increase with the extent of recycling. In the absence of removal treatments, the steady-state concentration of a dissolved solid entering the water system by process contact increases inversely with decreased blowdown. As systems are tightened extensively, they may become supersaturated with respect to one or more scaling reactions. In this communication, some experiments on the formation and growth of carbonate scales are described, some procedures for the prevention of scaling are outlined, and the feasibility of sensors for the prediction of instability are discussed. The complexities of scaling reactions and treatment procedures are such that no universal solutions are available(1). In fact, it may be said that each industrial system has unique features that require special considerations. However, there are some concepts that may be applied to all such systems.

Three general options are available for the prevention of undesirable scaling. They may be summarized as follows:

- Use of pH control, inhibitors, and blowdowns to maintain the steady-state dissolved solid concentrations in tolerable ranges.
- Removal of dissolved (and suspended solids) by pH control, additions, precipitation, settling, clarification, and related treatments to prevent critical supersaturation.
- Inducement of scale formation in localized regions where it can be tolerated and conveniently removed periodically.

Experiments on scale structure and growth rate and the development of stability sensors are essential in the advance of all three options.

EXPERIMENTS ON CARBONATE SCALES

During the past two years, experiments have been performed to determine the effects of several important variables on the formation and growth of carbonate scales in flowing systems. Figures 1 and 2 are schematic diagrams of the water flow system and the test cell wherein scaling was induced by controlled temperature gradients.(2) At flow rates of about 10 l/m, the growth of carbonate scales on several rings of stainless steel (T302) were studied. A series of heaters and thermocouple-controller circuits were used to maintain the desired temperature gradients. The composition of the circulating water was adjusted by means of chemical additives for pH and ion concentration control, additions of suspended solids, and bubbling of CO_2/ Argon mixtures to equilibrate the water with particular values of the partial pressure of carbon dioxide. Only several representative features of the experimental work will be discussed.

The regions of predominance of calcite, aragonite, and vaterite are shown in Fig. 3 from the work of Roques and Girou.(3) These data are of particular importance in analysing the results of the thermally-induced scales formed in the present experimental work. Figs. 4 and 5 are representative photomicrographs taken in a JEOL-JXA-35 scanning electron microscope equipped with EDAX-9100 analytical equipment. Structural analyses were also performed by conventional X-ray diffraction. In Fig. 4, the formation of aragonite crystals (a) on a layer of iron chloride and (b) on the stainless steel substrate from water to which fine particles (minus 320 mesh) were added. In general, the presence of an iron chloride layer inhibits carbonate scale formation and blunts the aragonite needles. The presence of suspended iron oxides caused a shift from predominantly hexagonal calcite to predominantly orthorhombic aragonite deposits. In Fig. 5, representative mixtures of calcite and aragonite in the absence of an iron chloride layer are shown. The principal conclusions from these structural studies are summarized as follows:

- At substrate temperatures less than 50°C, calcite tends to be the predominant form; at temperatures greater than 60°, aragonite tends to be predominant; between 40° and 60°C, transient vaterite can be observed occasionally.
- The presence of Mg^{++} ions promotes the formation of aragonite.
- The presence of Fe^{++} ions tends to suppress carbonate crystal formation, in part through the formation of an adherent iron chloride layer.
- Addition of iron oxide powder has little effect on either the structure or growth rate of carbonate crystals.

A number of other interesting effects have been observed in the formation of carbonate crystals. As expected, high flow rates and high substrate temperatures favor aragonite formation. At higher Mg^{++} concentrations, dolomitic carbonates and hydrated carbonates were observed. The specific effects of some of the operating variables on growth rates are described in the following section.

For illustration, the rate at which thin scale deposits form at times up to about 15 hours are shown in Figs. 6 and 7. These data are presented

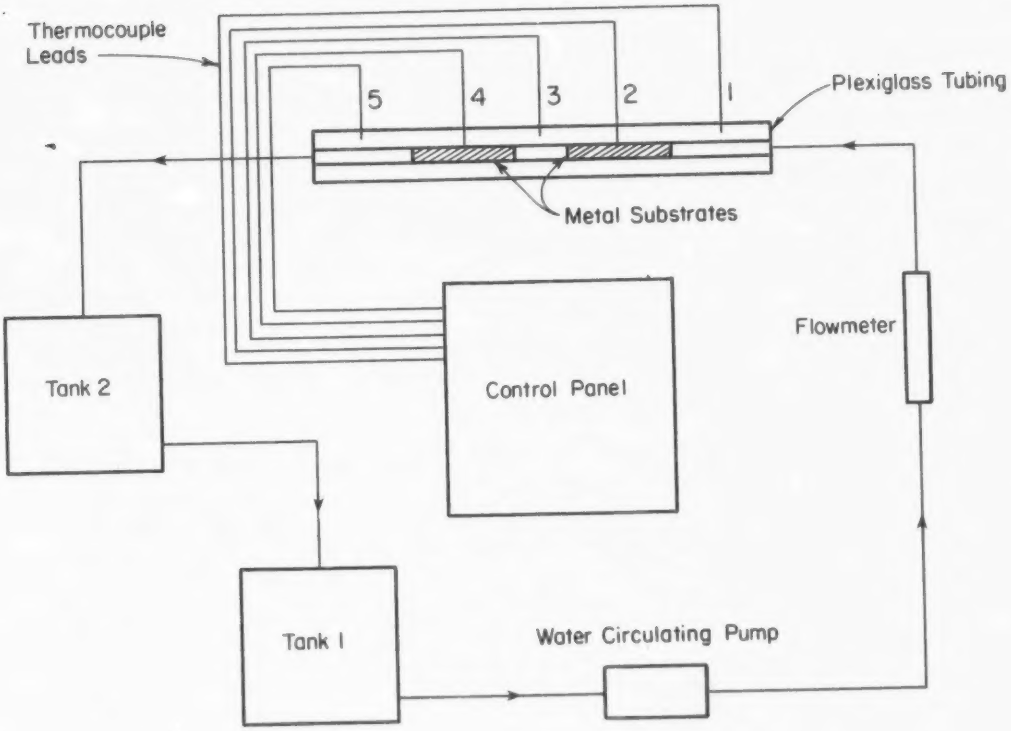
Thermocouple Leads
5
4
3
2
1
Plexiglass Tubing
Metal Substrates
Flowmeter
Tank 2
Control Panel
Tank 1
Water Circulating Pump

Figure 1. Schematic Diagram of Flow System

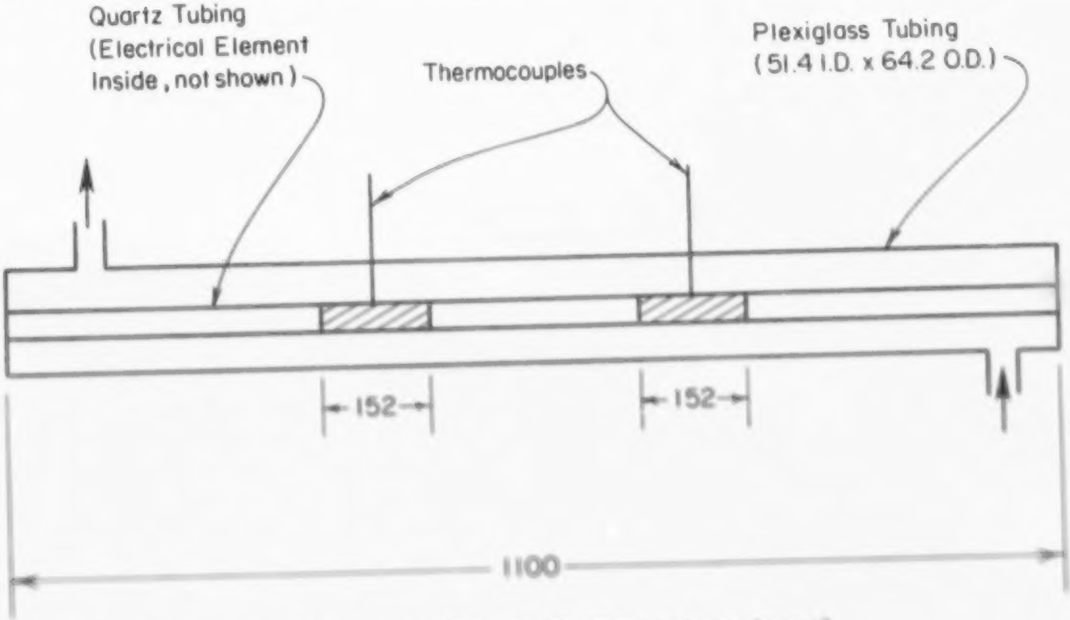
Quartz Tubing
(Electrical Element
Inside, not shown)
Thermocouples
Plexiglass Tubing
(51.4 I.D. x 64.2 O.D.)
152
152
1100

Figure 2. Schematic Diagram of Test Cell (Dimensions in mm)

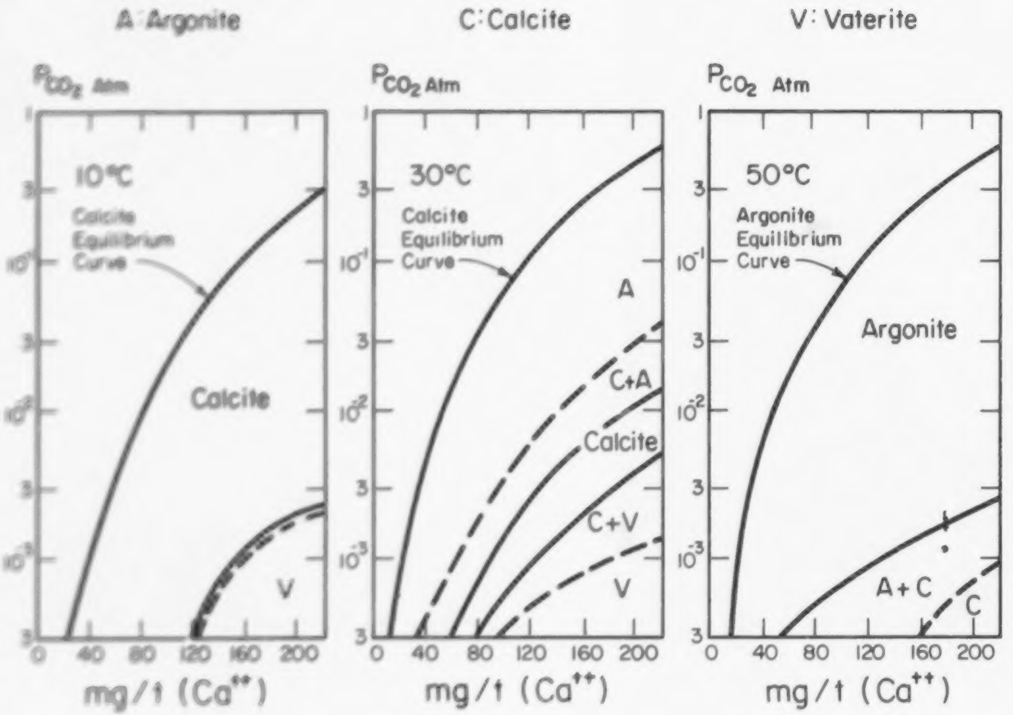

Fig. 3. Regions of Predominance of Structural Forms of Calcium Carbonate.

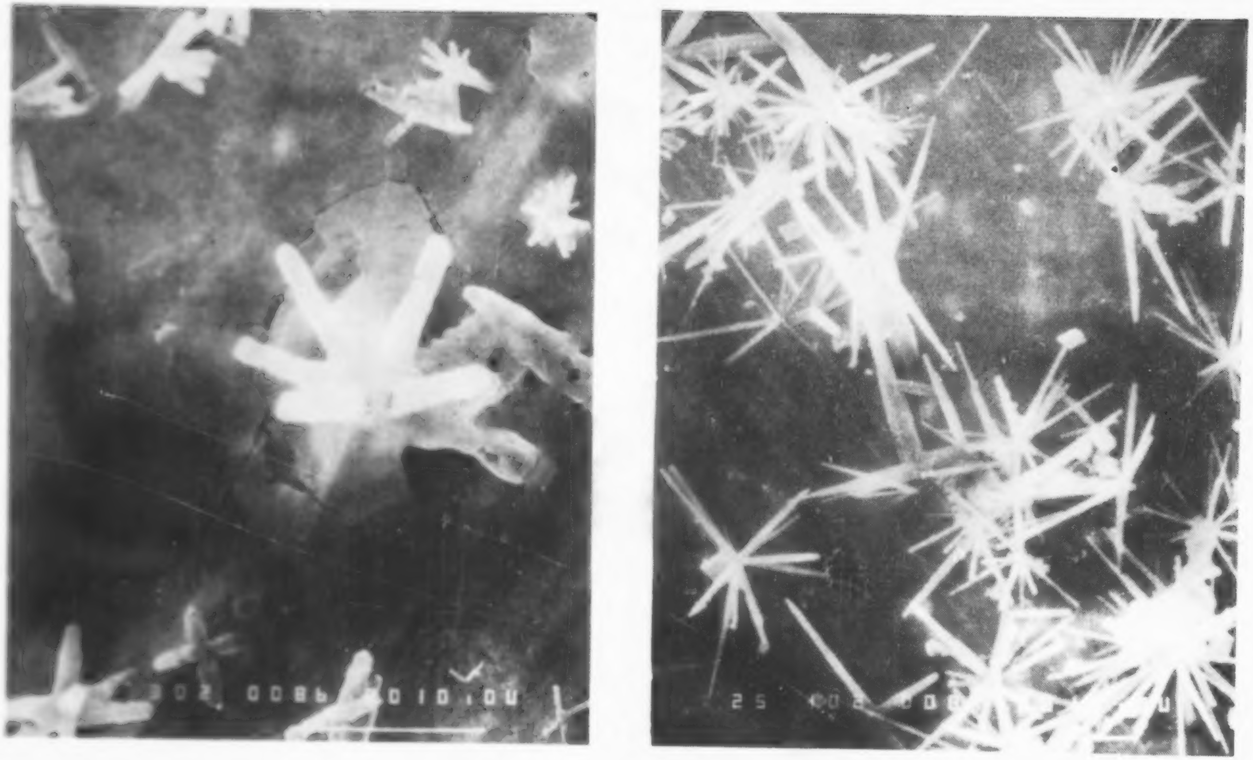

Fig. 4. Scanning electron micrographs of carbonate crystals. Left: Aragonite crystals on iron chloride substrate at 3000X; Right: Aragonite and calcite crystals on stainless steel with particles of iron oxide at 1000X.

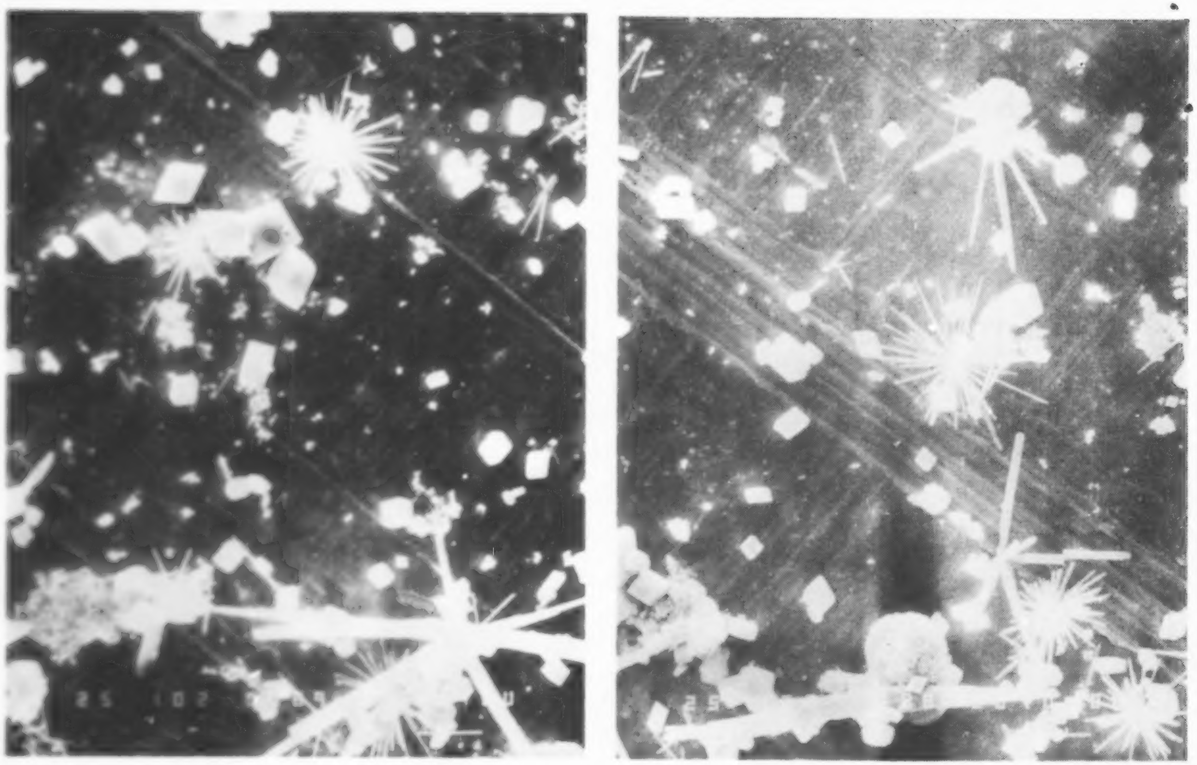

Fig. 5. Scanning electron micrographs of aragonite needles and calcite crystals with iron oxide powder on polished stainless steel substrate at 1000X.

as graphs of weight gain per unit area versus the square of time because it has been found that the data correlate well with a "parabolic growth model." After a variable incubation time, the rate of growth is inversely proportional to current scale thickness. The conditions for Figs. 6 and 7 were approximately identical except that in the case of the data of Fig. 7, one half of the Ca^{++} ions were replaced with Mg^{++} ions. In Fig. 8, the parabolic growth rate constant is shown as a function of $CO_3^{=}$ concentration expressed as the difference between the carbonate concentration at the interface and the carbonate concentration in the bulk solution. It was found that this driving force was most influential in determining the scale growth rate.

AVOIDANCE OF SCALE FORMATION

The avoidance of carbonate scale formation in recycled blast furnace top gas scrubber water serves as an excellent example of one type of scale avoidance problem. The problem has been discussed in this symposium by Nemeth and Wisniewski.(4) One approach to the scaling problem that has been suggested by Brower, Luther, and Ryckman(5) is to lower pH of the scrubber water by the addition of waste acids from pickling solutions. If the acid addition is made prior to the clarifier several benefits might occur. In addition to the removal of excess basic (Ca, Mg) carbonates, the iron content of the waste acids may promote flocculation and settling in the thickeners and also lower the cyanide content by the formation of iron cyanide complexes.

Inherent in this type of control procedure is the need to avoid serious corrosion problems as well. Close control of water chemistry established by the use of reliable sensors is a necessary feature in the recycling of contact process waters.

SENSOR DEVELOPMENT

There are many approaches that may be taken in the development of sensors for process control. A few examples are given as follows:

- Specific ion electrodes
- Thermal gradient devices
- Partial pressure sensors for CO_2, O_2, etc.
- Surface property of coupon devices
- Accumulated mass devices
- Direct saturation index devices.

At present, specific ion electrodes including pH measurement and standard coupons are the only methods to be used extensively other than direct periodic sampling and analysis. In the experiments described briefly in this report, it has become clear that devices based on thermal gradient measurement and those based on CO_2 partial pressure measurement might be used successfully in relatively clean, e.g. laboratory, conditions. If these devices can be applied to industrial water systems, it would be possible to introduce automatic equipment for treatment additions and blowdowns.

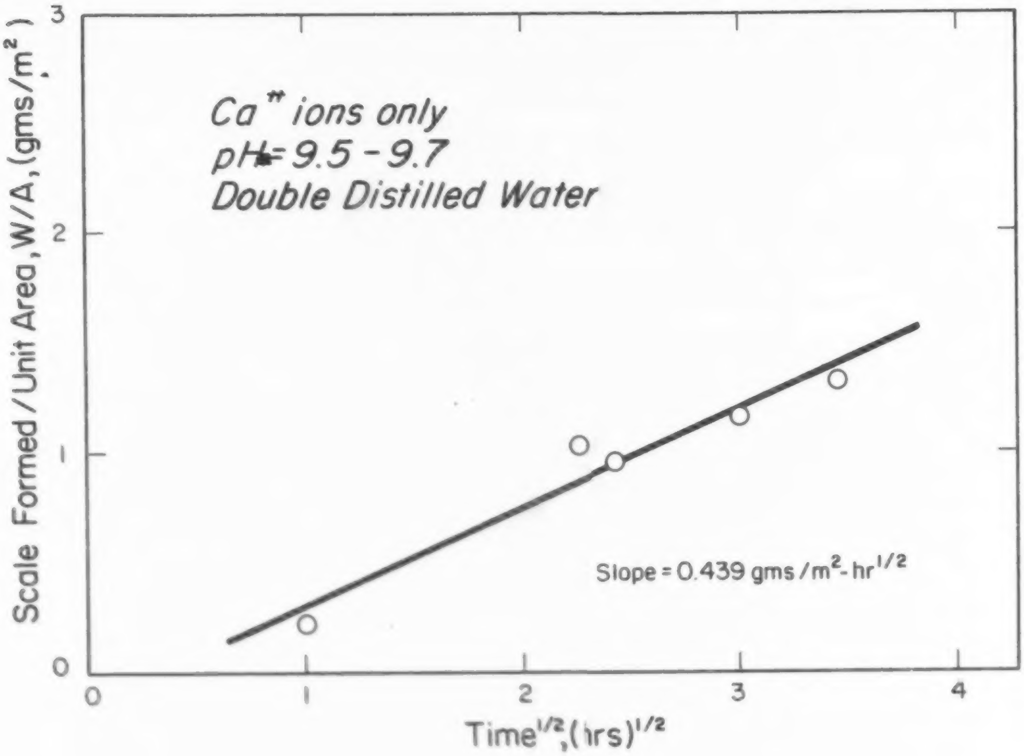

Fig. 6. Scale Formation on Stainless Steel Substrate
P_{CO_2} = 0.36 atm; Ca^{++} = 22 ppm; Bulk Temp = 47°C;
Surf. Temp = 70°C.

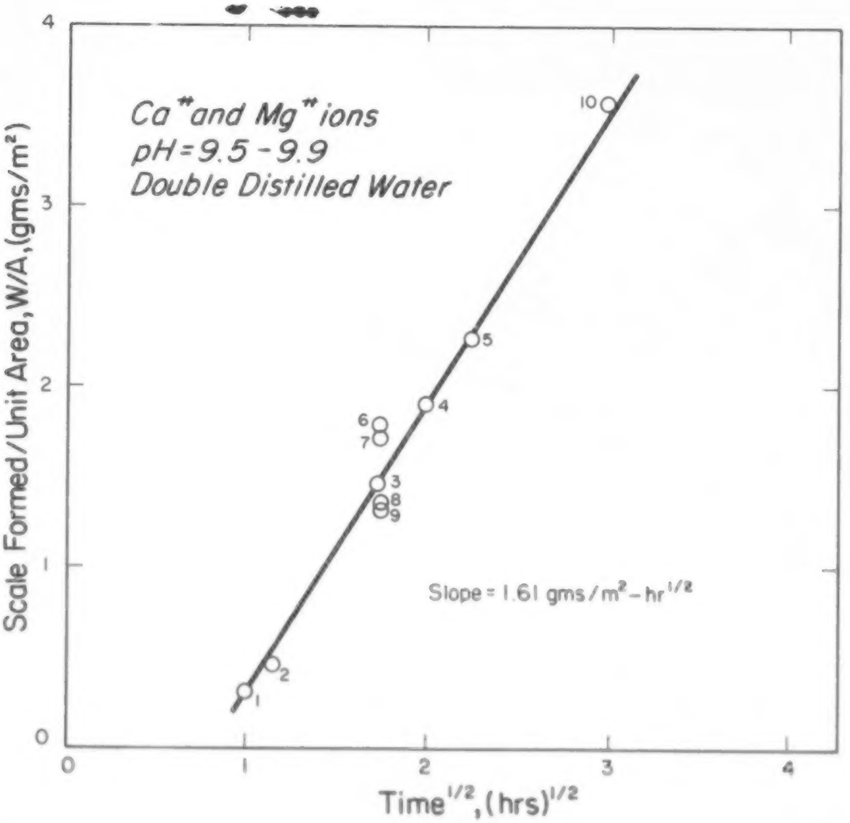

Fig. 7. The Influence of Mg^{++} on Scale Formation.

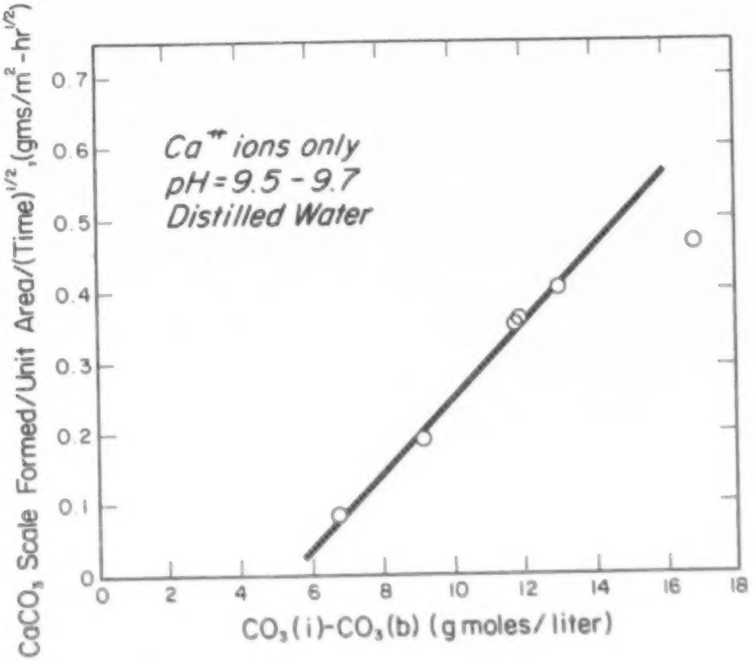

Fig. 8. The Influence of Carbonate Concentration on Parabolic Rate Constant.

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REDUCTION OF WASTES DISCHARGED FROM STEEL MILLS IN METROPOLITAN CHICAGO THROUGH LOCAL ORDINANCE ENFORCEMENT

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INTRODUCTION

The Metropolitan Sanitary District of Greater Chicago (District) was organized in 1889 and under its current charter, has the responsibility of providing sewage collection and treatment service for an area of approximately 860 square miles, including the City of Chicago and approximately 130 surrounding communities. The District serves a connected domestic population of about 5.5 million, plus an industrial sector with a waste load equivalent to about 4.5 million population. The District operates and maintains seven wastewater treatment plants that treat approximately 1.5 billion gallons per day of combined industrial and domestic wastewaters. All of the plants are biological activated sludge systems, with some including biological nitrification and dual media filtration.

These plants receive flow from over 500 miles of intercepting sewers and 5,000 miles of local sewers. The District is also responsible for enforcing applicable State and Federal water quality regulations along 72 miles of navigable inland waterways, over 200 miles of small rivers and streams, and 36 miles of Lake Michigan shoreline.

INDUSTRIAL ACTIVITIES WITHIN DISTRICT

A substantial amount of industrial activity is conducted within the District area. This activity covers a wide spectrum, from iron and steel manufacturing to household appliances. Out of approximately 12,000 industries within the District area, 6,000 are classified as wet industries, that is, discharging some process wastewater and/or cooling water.

Cook County, which is approximately the same area as served by the District, is the most productive county in the United States in terms of manufacturing activity. Total shipments of manufactured goods out of Cook County in 1979 amounted to $56,086,000,000 from 5,654 plants with 20 or more employees. Some of the largest manufacturing industries in Cook County include; organic chemical, miscellaneous plastic products, blast furnaces and steel mills, paints and allied products, telephone and telegraph apparatus, metal cans, motor vehicles and passenger car bodies, radio and television receiving sets, and confectionery products among others.

INDUSTRIAL WASTE CONTROL PROGRAM

The District is one of the few municipal sewage treatment agencies with a long and effective record of enforcement regarding discharge of industrial wastes to the public sewer system and to the waterways. On July 13, 1962, the board of Trustees of the District adopted an Industrial Waste Ordinance that set forth certain limiting conditions for the discharge of liquid industrial wastes into the sanitary sewer system. Contained as part of these conditions were the limits for pH not to be lower than 4.5 or higher than 10.0 and fats, oils, and greases not to exceed 100 mg/l.

The Illinois Sanitary Water Board, the predecessor of both the Illinois Pollution Control Board and the Illinois Environmental Protection Agency, on June 28, 1967, adopted regulations for water and effluent quality for discharge to waters in the State of Illinois. On January 28, 1968, the United States Department of the Interior approved the Illinois standards and they became law in the State of Illinois on April 1, 1968.

Subsequent to the passage of these State regulations, the District determined that a new industrial waste ordinance was needed to further control the discharge of industrial waste into the sewer system. The purpose of this ordinance was to insure that the quality of effluent from the District treatment plants would meet the new standards for discharge to the waters of the State. An Advisory Committee, consisting of representatives from industry, consulting engineering firms, the academic community, and the District, was appointed to develop a new industrial waste ordinance. The charge given to the Advisory Committee was to develop an ordinance that would insure that the effluent from the District's treatment plants would meet the new regulations set by the Illinois Sanitary Water Board, protect the treatment plants from upsets, and allow industry ample latitude with regard to the type of pretreatment systems necessary to control the quality of industrial wastes discharged to the sewer system.

On September 18, 1969, the Board of Trustees of the District adopted the Sewage and Waste Control Ordinance which set specific industrial discharge limits for 13 contaminants and 9 limiting conditions on discharges to sewers and limits on 25 contaminants and 2 limiting conditions on discharges to waterways.

Enforcement of the Ordinance has been delegated to the Industrial Waste Division (Division) of the District which is responsible for monitoring the discharge from over 6,000 industries within the District's jurisdiction. Two groups in the Division, a field unit consisting of 28 Pollution Control Officers, 2 Sanitary Engineers, and 34 Water Samplers; and an enforcement section consisting of 4 Pollution Control Officers and 2 Sanitary Engineers, administer the Ordinance. Since pollutants can be most effectively controlled at the point source of generation, continued inspection, monitoring and sampling of industrial effluent discharge is required before industrial wastes enter the sewer system. The field unit performs the physical inspections and sampling of industrial facilities while the enforcement section handles the administrative processes required when a company fails to meet compliance with the specified discharge limits. A laboratory group consisting of 3 Sanitary Chemists and 16 Laboratory Technicians provide analytical support for the enforcement responsibility.

Field surveillance and monitoring activities include complete inspections of industrial facilities to determine: the nature of the industrial operations; the types of wastes generated; waste pretreatment processes employed; type, volume and storage of sludge and/or process residue generated for disposal, method and frequency of removal; identification of both hauler and disposal facility for sludge and/or process residue disposal; water consumption information; and plant layout of all floor drains, sewers and sampling locations. With this information, along with knowledge of the production and clean-up hours of the facility, a sampling program is designed to obtain representative samples of the industry's sewer discharge. An industrial facility can be sampled by: (1) 24-hour sampling trailer utilizing flow measuring equipment, if necessary; (2) automatic sampling by either battery or vacuum operated samples on an 8- to 24-hour basis; (3) manual sampling of 1- to 8-hour composite or grab sampling; or (4) single grab sampling.

INDUSTRIAL WASTE ENFORCEMENT

Using the results of field inspections and samplings, an on-going review is conducted of the status of compliance with the Ordinance of the numerous industrial facilities and other dischargers to the waterways and sewers in the District's jurisdiction. When a company is in violation, representatives appear for a conciliation meeting. The company is required to submit a plan and schedule for compliance with the Ordinance. The company is encouraged to use good housekeeping techniques, procedural and chemical changes, etc., to reduce its pollutant discharge to the sanitary sewerage system. If necessary, pretreatment equipment must be installed. Conciliation continues so long as the company is making a good faith effort toward compliance.

When conciliation is no longer productive, Show Cause proceedings are recommended. Show Cause is and adversary proceeding with parties represented by counsel. The offending discharger is ordered to comply with the Ordinance by a specific date. If the order is not complied with a lawsuit is filed, seeking compliance through injunction and penalties through fines.

CONTROL OF STEEL MILL POLLUTION

Included in the District's jurisdiction are five major steel making facilities, all located within a 10-mile reach of the Calumet River. The facilities have a combined total production capacity of 7,800,000 tons of steel per year. One of the District's major water pollution enforcement activities is in the area of steel mill wastes. Enforcement work with the steel mills began in 1969, at which time these five facilities were discharging industrial wastes into the Calumet River and Lake Michigan from 45 separate outfalls. See Figure 1.

CONDITIONS IN 1969

The five steel mills had a total of 45 outfalls discharging to the Calumet River system in 1969. The number of outfalls from each mill is as follows:

	Steel Mills					
	A	B	C	D	E	Total
Number of outfalls	9	6	5	7	18	45

The combined total quantities of flow and contaminants from these five mills in 1969 are expressed as a daily average and shown as follows:

Parameters	Quantity
Liquid Volume	546,000,000 gallons
Suspended Solids	166,000 pounds
Iron	25,000 pounds
Ammonia	5,150 pounds
Oil and Grease	39,500 pounds
Phenols	268 pounds
Cyanide	376 pounds

Detailed breakdown of the above quantities for each of the five mills is shown on Table 1.

The Calumet River has a net flow away from Lake Michigan. Fluctuations in the water level of Lake Michigan cause short term reversals in flow, especially toward the lakeward end of the Calumet River. The O'Brien Lock, as shown on Figure 1, is operated in such a fashion so as to cause a relatively small, but steady flow away from Lake Michigan.

Compared to the volume of waste discharged by the steel mills, the river's net flow is incapable of preventing industrial waste from these steel mills from flowing into the lake. The comprehensive revision and amending of the District's Sewage and Waste Control Ordinance in 1969 incorporated the State of Illinois waterway effluent standards. These standards gave the District the authority to initiate action to bring these steel mills into compliance with Illinois effluent quality standards.

ENFORCEMENT ACTION AND PROGRESS

The District initiated enforcement in 1969 following sampling of all five steel mills. Samples were taken each hour for 24 hours each day over a ten day period. The hourly grab samples were composited into daily composite samples for each outfall. These samples were taken to the District laboratory for analysis. The analysis indicated that the discharges for the steel making facilities were in violation of the District Sewage and Waste Control Ordinance. Enforcement procedures were initiated against the steel mills.

In the matter of each of these five steel mills, conciliation proceedings eventually broke down for various reasons and Show Cause action was initiated. The Show Cause hearings resulted in the Board of Commissioners passing orders requiring all five steel mills to have their industrial waste discharges in compliance with the Sewage and Waste Control Ordinance by specific dates. It became apparent to the District during the conciliation and show cause hearings, that only a lawsuit would cause the corporate management of the various steel mills to commit the necessary capital and operating funds to this type of program. The steel mills did not comply with the Order of the Board of Commissioners and as a result separate lawsuits were filed against each steel mill in the Circuit Court of Cook County. In each of the five lawsuits, the court proceedings and conferences resulted in a consent decree and a compliance schedule for each steel mill for the reduction of the pollution loading to the Calumet River.

The nature of the wastes being discharged by mills to the Calumet River system dictated the following requirements as being desirable in achieving compliance.

(1) Separate process waste from cooling water so that cooling water could be returned to the river as noncontact.

(2) Reduce or eliminate the liquid volume of process waste being discharged to the river.

(3) Provide process waste treatment systems to reduce the constituent concentrations to within the waterway effluent standards for waterway discharge or within the sewer discharge limits for disposal to the sewer.

Separation of cooling water from process waste was a reasonable and practicable request. This would achieve a large reduction in the liquid volume of process waste being discharged to the river. To further reduce the liquid volume of process waste, and to achieve a measure of water conservation, a significant amount of recycling should occur.

A major problem facing the technical personnel of the various steel mills involved in the pollution control programs was the age and condition of much of the mill facilities. At the time, most of the mill facilities were in excess of 30 years in age, and as a result there was insufficient information on the location of underground drainage, pipelines, and other facilities. In addition, the age and condition of the production facilities was such that a major expenditure of funds for pollution control and the need to install new equipment in old facilities warranted some modernization of the production facilities.

In 1969, the steel mills were found to employ the basic treatment processes of skimming for oil removal and clarification for solids removal. However, due to the age of facilities and an apparent lack of maintenance, these facilities were found to be ineffective and often not capable of efficient operation. Breakdowns, outages, and overloading were common operational problems.

The principal means of improved treatment for wastes from the steel mills would consist of skimming for oil and grease removal, clarification for solids removal, and filtration to achieve a final high degree of removal of solids and oil and greases to facilitate recycling. In a few cases, separate process treatment for other constituents, principally cyanide, needed to be employed, in order to meet the limits for discharge to the sanitary sewer system or waterway. For some constituents, such as ammonia and suspended solids, specific reduction was not required if discharged to the sewer. The reason for this is that District treatment plants presently have, or are scheduled to have, the capability to treat and remove suspended solids and ammonia.

ABATEMENT PLANS FOR EACH STEEL MILL FACILITY

Steel Mill A. The major production facilities at Steel Mill A that generate industrial waste and the waste treatment systems installed are:

(1) Five blast furnaces from which the wastewater streams are directed to clarifiers, cooling towers and then recycled. The blowdown from this recycle system is used as quenching water for slag.

(2) Plate mills and structural mills from which the wastewater flows through scale pits, oil separators and then to a central wastewater treatment facility which consists of three high rate reactor clarifiers, cooling towers, sludge thickener, and a vacuum filter. The treated effluent water is then recycled back to these mills for reuse.

(3) Wastewaters from four electric furnaces and the basic oxygen process shop pass through a first stage clarifier and then flow to the central wastewater treatment facility for processing and recycle.

(4) Sintering plant wastewater which also flows to the central wastewater treatment facility for processing and recycle.

Steel Mill A has stopped the discharge of process wastewater to any waterway and is now in a 100 percent water recycle and reuse mode. From 4.5 to 5.0 MGD of blowdown now goes to the District for treatment.

Steel Mill B. The major production facilities at Steel Mill B that generate industrial waste and the waste treatment systems installed are:

(1) A coke battery that consists of 45 ovens. The wastewaterwater from these facilities is recycled; the blowdown from the recycle system passes through a settling basin, an oil skimmer, and then discharges to the sanitary sewer.

(2) The basic oxygen process shop, consisting of two 120-ton vessels. Wastewater flows are recycled; the blowdown passes through settling basins and then to the District.

(3) The blast furnace plant. Wastewater passes through clarifiers, an alkaline chlorination cyanide destruct process, and deep bed sand filters. This flow is then recycled as noncontact cooling water for the blast furnace plant or the rolling mills and then discharged to the Calumet River.

(4) Blooming and rolling mills. Process wastewater passes through scale pits, oil separators, and deep bed sand filters and is recycled as noncontact cooling water and eventually discharges to the Calumet River.

Steel Mill B has reduced the number of outfalls to the Calumet River from six in 1969, to one outfall discharging treated process water which has been used for cooling. In 1980, this mill was closed due to business reasons.

Steel Mill C. The major production facilities at Steel Mill C that generate an industrial waste and the waste treatment systems installed are:

(1) The coke plant, consisting of 100 ovens. Wastewater flows are

partially recycled, with the blowdown going through a clarifier, oil separator, cyanide stripper and then discharging to the sanitary sewer. Noncontact cooling water is pumped from and discharged to the Calumet River.

(2) Blast furnace and sintering plant. Wastewater flows through clarifiers, cooling towers, and are then used for gas scrubbing. Blowdown from this system goes to the sanitary sewer. This mill has reduced the number of outfalls from five in 1969 to three for discharging noncontact cooling water in 1980.

Steel Mill D. The major production facilities at Steel Mill D that generate an industrial waste and the waste treatment systems installed are:

(1) One blast furnace. Process waste treatment consists of oil skimmers, clarifier with chemical treatment, and a vacuum filter. This treated flow is then diverted to cooling towers and recycled. Blowdown is discharged to the sanitary sewer.

(2) Coke plant, consisting of 75 ovens. Process wastes pass through a waste treatment system consisting of oil skimmers, clarifier with chemical treatment, and a vacuum filter. The blowdown is used for quenching push coke in a closed loop system.

(3) By-product plant. Process wastes are diverted to the sanitary sewer system. Noncontact cooling water is pumped from and discharged to the Calumet River.

(4) Basic oxygen furnace shop, rolling mills, tube mills, and wire mills. Process wastes are treated through deep bed filters and recycled. The filter backwash is treated in a waste treatment system. This mill has reduced the number of outfalls to the Calumet River from seven in 1969, to one in 1980.

Steel Mill E. The major production facilities at Steel Mill E that generate an industrial waste and the waste treatment systems installed are:

(1) The basic oxygen process shop, consisting of two, 100-ton units. Process wastewaters are diverted to clarifiers, cooling towers and recycled in a closed loop system. Blowdown is used for slag quenching with no discharges.

(2) Primary mills. Wastes are discharged to three settling pits which prior to 1970 discharged to the Calumet River. This is now a closed loop system with the discharge being returned to the mill for recycling use. The blowdown from the mill goes to a pump station and then to a sanitary sewer. Noncontact cooling water is pumped from and discharged to the Calumet River.

(3) The hot strip mill. Process waste goes to a sand filtration system, with treated water recycled back to the mill for reuse.

(4) All pickling wastes are treated through a waste treatment system with the final effluent going to the sanitary sewer.

(5) Cold mill. Wastes are treated through an oil emulsion system. Wastes from the blowdown tanks are sent back to the pickling waste treatment system. Oil is scavenged out.

(6) Galvanizing and electroplating wastes are treated through the pickling waste treatment system.

Steel Mill E has reduced the number of outfalls to the Calumet River from eighteen in 1969 to four noncontact cooling water outfalls in 1980.

IMPACT ON THE WATERWAY

For six parameters (suspended solids, iron, ammonia, oil and grease, phenols, cyanide), reduction in the pollutants discharged to the waterways has averaged 100 percent from the five steel mills discharging to the Calumet River and Lake Michigan. Discharges that have been diverted to the District sanitary sewer systems are frequently monitored and are at present in compliance with the District Sewage and Waste Control Ordinance.

A summary of total reduction in discharge to the waterways from these five steel mills from 1969 to 1980 is shown in the following table. Quantities are expressed as daily averages.

Parameter	Units	1969	1980	Percent Reduction
Liquid Volume	MG	546	0	100
Suspended Solids	lbs.	166,000	0	100
Iron	lbs.	25,000	0	100
Ammonia	lbs.	5,150	0	100
Oil & Grease	lbs.	39,500	0	100
Phenols	lbs.	268	0	100
Cyanide	lbs.	376	0	100
Number of outfalls		45	9	80

Examination of water quality data for the eleven-year period from 1970 through 1980 has been made to determine the impact of these dramatic reductions on the quality of the receiving waterway.

The District performs routine monitoring of the entire waterway system under its control. Two of the stations which are routinely monitored are within the reach of waterways which are influenced by four of the five steel mills. These stations are at the Ewing Avenue and 130th Street Bridges over the Calumet River as shown on Figure 1. The District's routine monitoring of the waterways consists of monthly grab samples taken at these bridges, analysis of these samples and reporting of analytical results.

In the reach of the Calumet River between its mouth at Calumet Harbor and the O'Brien Lock, the steel mills comprise the principal inflow. There are few combined sewer gravity overflows and only one combined sewer storm pumping station in this reach. Their frequency of discharge to the river is low and their impact on receiving water quality is minor compared to the output of the steel mills.

As to the impact of Steel Mill E on the Little Calumet River, this is more difficult to judge by receiving waterway data, as the reach of the river to which this steel mill discharges also receives discharges from numerous combined sewer outfalls, a combined sewer storm pumping station and a major municipal sewage treatment plant.

As shown on Table 1, discharge to the Calumet River of process flow and a number of chemical constituents has ceased. As indicated earlier in the discussion, the desirable objectives of the enforcement action included separation of process water and cooling water flows, a reduction of process flows and treatment of process waste flows. These have been accomplished. As a measure of overall achievement of the enforcement program and pollution abatement plans implemented by the steel mills, Figures 2 and 3 show significant improvement in both dissolved oxygen and temperature. Over the eleven-year period, the annual average dissolved oxygen increased from 6.9 mg/l in 1970 to 11.2 mg/l in 1980 at Ewing Avenue and from 6.4 mg/l to 10.0 mg/l at 130th Street. Maximum and minimum values for each year have also shown improvement. The waterway standard for dissolved oxygen as established by the Illinois Pollution Control Board (IPCB) is not less than 2.0 mg/l prior to December 31, 1977, and not less than 4.0 mg/l after January 1, 1978. Nearly all values were in compliance with this standard. The minimum values in each of 1970 and 1978 fell below the standard during some months of both summers.

Similarly, the annual average temperature decreased from 18.2°C in 1970 to 10.7°C in 1980 at Ewing Avenue and from 17.5°C to 10.8°C at 130th Street. Annual averages within the period varied somewhat beyond these values, but there is, nevertheless, an overall trend toward lower average annual temperatures. Maximum annual temperatures varied considerably at both stations, ranging between 30.0°C and 17.0°C. No trend in annual maximum temperatures is evident. However, minimum annual temperatures show a definite trend toward lower values. The IPCB standard for temperature is not to exceed 34°C. No values at either Ewing Avenue or 130th Street exceeded this limit.

As shown by Figure 4, total suspended solids do not evidence a trend toward lower values, despite the reductions in suspended solids discharged to the waterway by the steel mills. This suggests that total suspended solids in the waterway are at a background level and were not significantly affected by reductions in discharge from the steel mills. Annual averages of total suspended solids varied between 20.8 mg/l and 10.8 mg/l at Ewing Avenue and between 27.3 mg/l and 15.2 mg/l at 130th Street. Annual maximum and minimum values at each station vary considerably without any apparent trend. The IPCB standard for total suspended solids is not to exceed 25 mg/l. All annual average values were below this standard, except for 1977 at 130th Street. At Ewing Avenue, many values in 1970, 1972, 1973, 1977, and 1980 were above this limit, whereas at 130th Street, the standard was exceeded in all years except 1980.

For ammonia nitrogen, the IPCB has established separate standards for summer and winter. For the months of April through October, the standard is not to exceed 2.5 mg/1, while for the months of November through March, the standard is not to exceed 4.0 mg/1. As shown by Figure 5, there were values which exceeded the summer standard in 1972 and 1973 at Ewing Avenue and in 1973 and 1978 at 130th Street. The annual average and minimum values at 130th Street and the annual minimum values at Ewing Avenue show a decreasing trend in the ammonia nitrogen concentration. The higher concentrations of ammonia nitrogen at both stations in the later years of the 1970 to 1980 period are not explainable by any records of discharge by the steel mills.

Elevated ammonia nitrogen concentrations in the latter part of the period are also evident in the winter data as shown on Figure 6. However, all values at both stations are well below the standard of 4.0 mg/1. Data for the winter period are less variable and suggest a trend toward lower ammonia nitrogen concentrations.

Fats, oils, and greases, over the eleven-year period do not evidence any trend. While the annual averages for both Ewing Avenue and 130th Street for the 1970 through 1979 period show a trend toward increasing concentrations, concentrations in 1980 are much lower than the several preceding years. As shown on Figure 7, the annual averages at both stations are quite close in magnitude and vary between a high of 25.3 mg/1 and a low of 5.3 mg/1. The annual averages for the year 1976 through 1979 exceed the IPCB standard of 15 mg/1 at both stations. The annual average at 130th Street in 1975 is also above the standard.

Some of the values for fats, oils, and greases at Ewing Avenue exceeded the limit in each of the eleven years. At 130th Street, all years except 1972 and 1980 had some values which exceed the standard. Effective November 23, 1977, the IPCB adopted a change in which further defined this standard. The change provides that this constituent "...shall be analytically separated into polar and non-polar components if the total concentration exceeds 15 mg/1. In no case shall either of the components exceed 15 mg/1 (i.e., 15 mg/1 polar materials and 15 mg/1 non-polar materials)." The District analyzes all effluent samples that exceed 15 mg/1 of total fats, oils, and greases for each of the components. However, this is not done routinely for waterway monitoring samples.

Total cyanide concentrations in the Calumet River at Ewing Avenue show a definite trend of improvement, whereas no trend is evident at 130th Street, as shown by Figure 8. The annual average total cyanide varied from 0.028 mg/1 in 1970 and 0.04 mg/1 in 1971 down to 0.004 mg/1 in 1980 at Ewing Avenue. At 130th Street, these annual averages varied between a high of 0.023 mg/1 and a low 0.005 mg/1 over the period of eleven years. During the last four years, the annual average steadily decreased at 130th Street. The IPCB standard for total cyanide was 0.025 mg/1 up until September 6, 1978. During this period of time, there were numerous values which exceeded the standard. Effective September 7, 1978, the standard for total cyanide was 0.1 mg/1. No values exceeded the standard subsequent to this change.

The record of improvement in the water quality of the Calumet River demonstrates that pollution control programs and expenditure of private and public monies do produce results. As shown by the data presented herein, the local enforcement program of the Metropolitan Sanitary District has caused five major steel making facilities to reduce their discharge of pollutants to the waterway and has caused improved water quality of the Calumet River.

TABLE 1. QUANTITIES OF FLOW AND CONTAMINANTS FROM FIVE STEEL MILLS IN 1969

Parameter	Units	Steel Mills A	B	C	D	E
Liquid Volume	MG	330	38	43	86	49
Suspended Solids	lbs.	69,760	13,800	14,300	48,200	20,200
Iron	lbs.	6,800	1,590	1,020	14,600	1,010
Ammonia	lbs.	1,600	650	1,070	1,080	745
Oil and Grease	lbs.	25,400	684	3,180	3,600	6,500
Phenols	lbs.	86	48	36	57	13
Cyanide	lbs.	150	11	42	67	3

Notes: Steel Mill B was closed in 1980 due to business reasons.
Quantities are expressed as daily averages.
Discharge of process flow and contaminants had ceased by 1980 for all steel mills. Therefore, all steel mills had achieved a 100 percent reduction in discharge of process flow and contaminants by 1980.

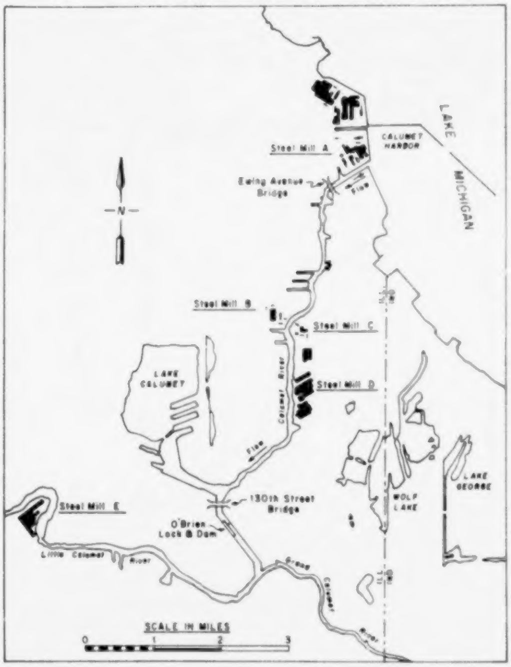
LAKE MICHIGAN
CALUMET HARBOR
Steel Mill A
Ewing Avenue Bridge
Flow
N
Steel Mill B
Steel Mill C
Steel Mill D
LAKE CALUMET
Calumet River
Flow
Steel Mill E
130th Street Bridge
O'Brien Lock & Dam
Little Calumet River
Grand Calumet River
WOLF LAKE
LAKE GEORGE
SCALE IN MILES
0
1
2
3

Figure 1. Steel Mills Located Along Calumet River and Little Calumet River

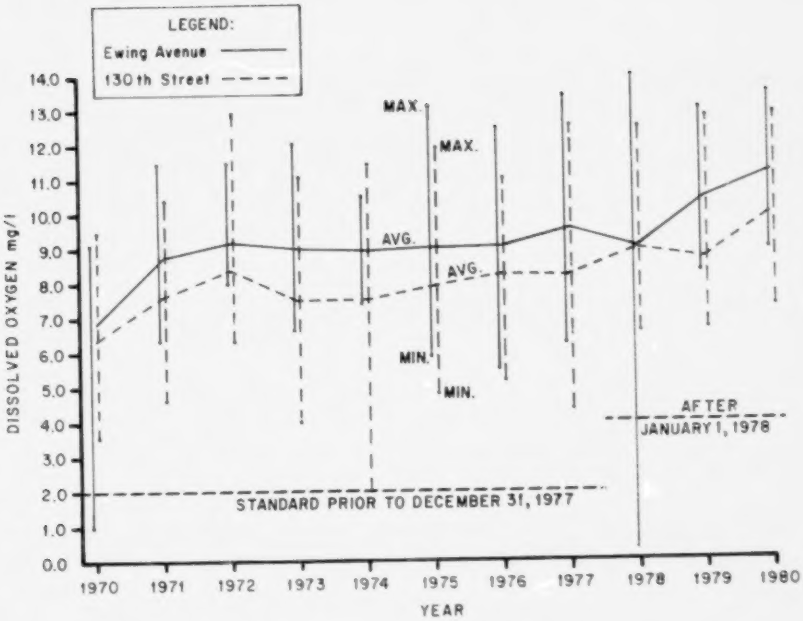

Figure 2. Calumet River Dissolved Oxygen Concentrations - 1970 thru 1980

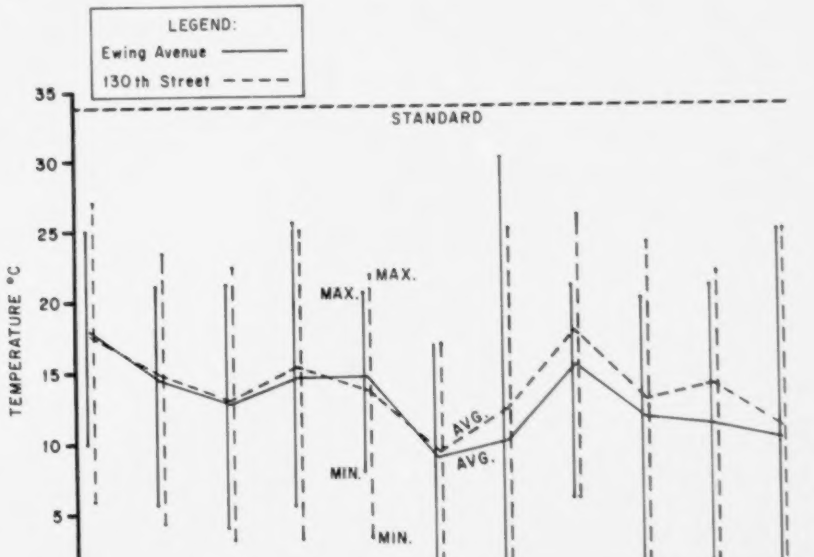

Figure 3. Calumet River Temperature - 1970 thru 1980

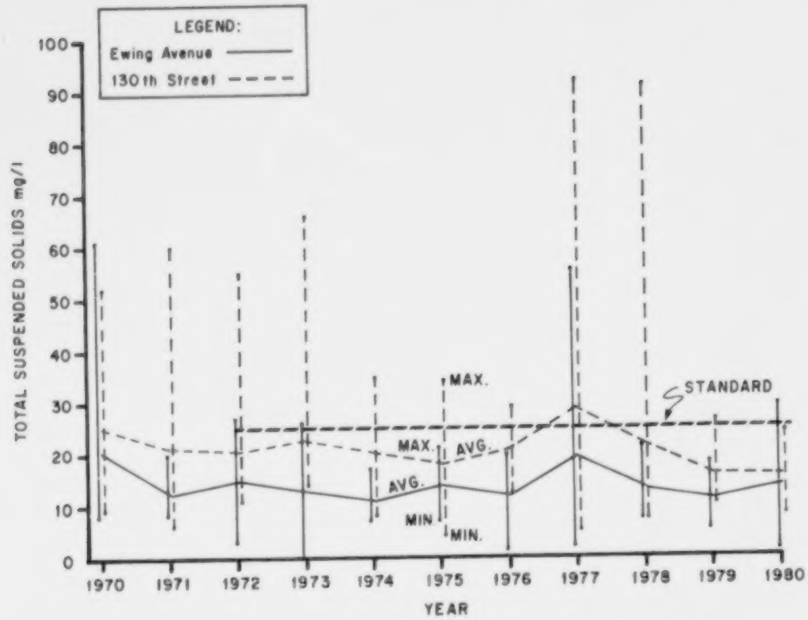

Figure 4. Calumet River Total Suspended Solids Concentrations - 1970 thru 1980

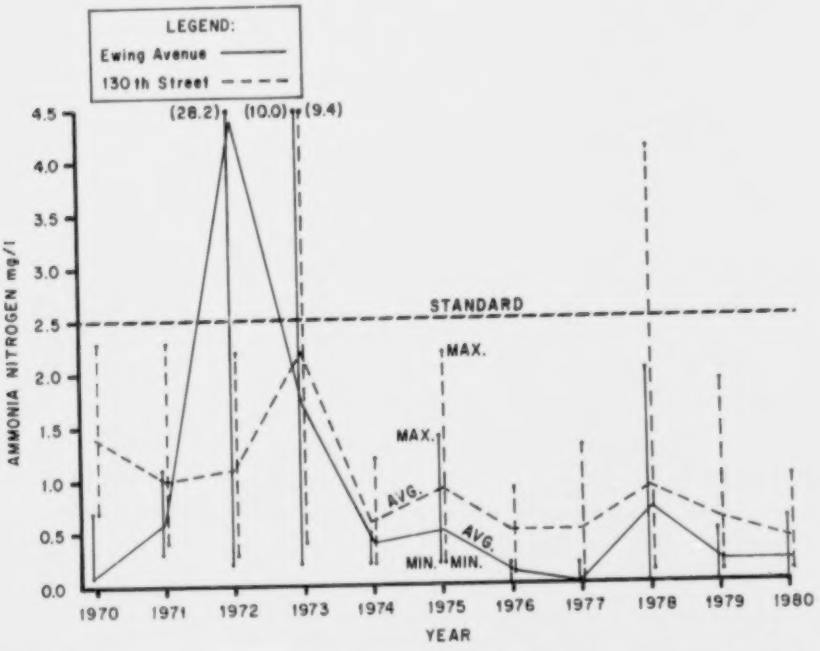

Figure 5. Calumet River Ammonia Nitrogen Concentrations - April thru October - 1970 thru 1980

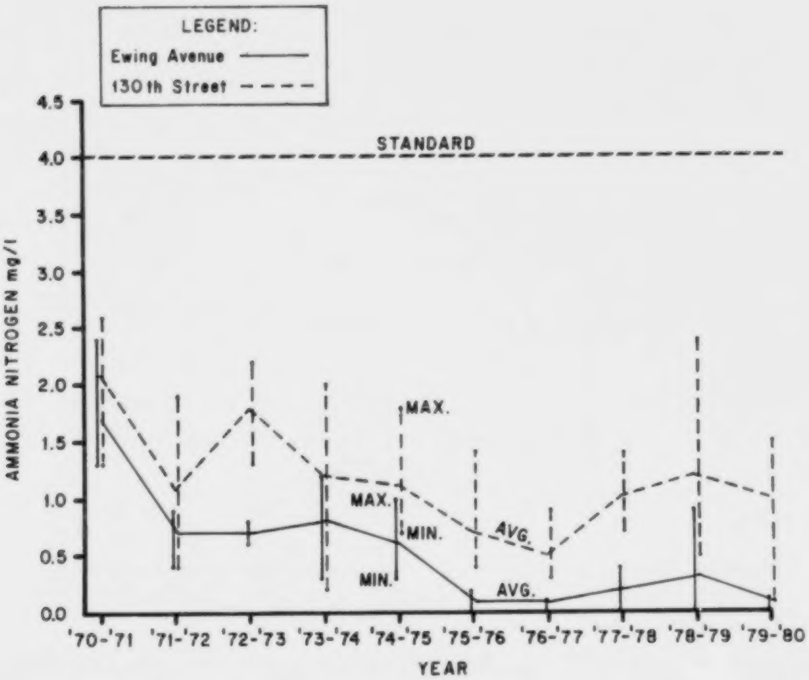

Figure 6. Calumet River Ammonia Nitrogen Concentrations - November thru March - 1970 thru 1980

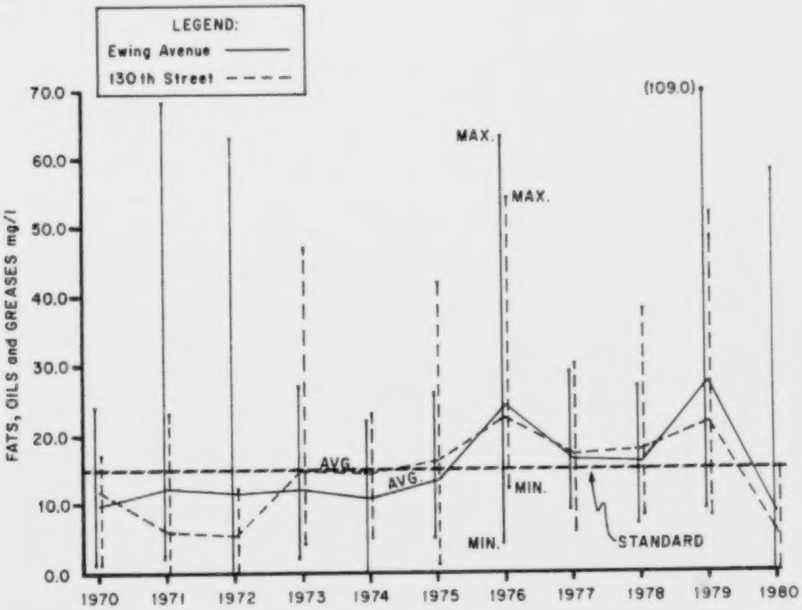

Figure 7. Calumet River Fats, Oils and Greases Concentrations - 1970 thru 1980

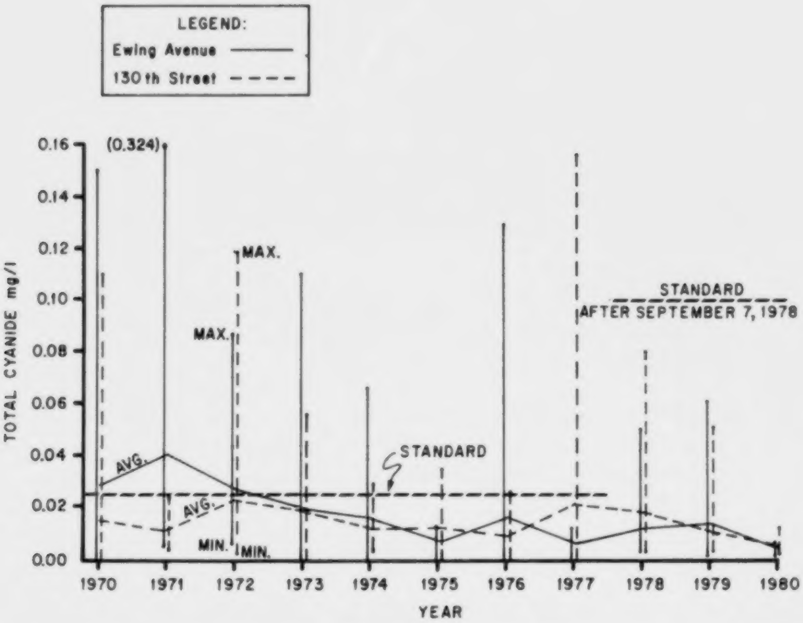

Figure 8. Calumet River Total Cyanide Concentrations - 1970 thru 1980

A MASS BALANCE MODEL FOR RINSEWATER IN A CONTINUOUS STRIP HALOGEN ELECTROLYTIC TINNING OPERATION FOR USE IN EVALUATING WASTEWATER TREATMENT AND RECOVERY ALTERNATIVES

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ABSTRACT

The operation and rinsewater application of J&L's electrolytic tinning operation at Aliquippa are studied in order to specify a plating chemical recovery technology for wastewaters. The existing treatment method for wastewaters, hydroxide precipitation, is adequate to meet discharge limits, but economics favor a change that uses a form of recovery

A mathematical mass balance model is developed to predict rinsewater concentration changes as flowrates are varied. The relationships described by the model are tested and it is shown that the model for tin is followed within a narrow margin of error. The significance of this is that wastewater flow (and mass rate of tin in the wastewater) can be measurably reduced with no apparent product defects.

The model is refined to reflect the installation of rinsewater controls that optimize rinsewater use, and various recovery techniques are applied to this refined model. A comparison of these recovery methods indicates that several alternatives exist that can recover plating chemicals successfully and have capital recovery periods of less that one year. In summary, the importance of modeling in this type of application is paramount to successful recovery.

INTRODUCTION

The electrodeposition of tin onto steel is a simple concept to understand, but a difficult manufacturing process to effect in a competitive market. Numerous variables impact on the successful commercial production of tin plated steel or tin plate. Some basic variables are chemical compatibility of all raw material used, knowledge by the production force of the process and even simpler concepts such as market supply and demand.

The objective of this research is to develop and demonstrate a fundamental sound approach to the proper management of a process wastewater.

The tin plate manufacturing process requires a careful application of water for cleaning and rinsing, but this water must then be removed from the process to insure product quality within customer specifications. In most cases, the water is not reusable within the tinning process.

The Aliquippa tinning operation of the Jones & Laughlin Steel Corporation, presently transfers tin line wastewater to a treatment facility to remove chemicals for acceptable discharge of the water to the Ohio River. This facility, referred to as the Chemical Rinse Treatment Plant, was constructed in 1971. This facility treats a combined flow of 25 different waste streams from various operations including wastewaters from the tinning operation. The primary constituents in the waste stream from the tinning operation are tin and fluoride. It was found that tin and fluoride were entering the plant at rates of 770 and 1090 lbs./day respectively, and being wasted to sludge. At an ever-increasing price for tin, it is clear that an economic recovery evaluation of the tin line waste streams is warranted.

ALIQUIPPA'S TIN PLATING PROCESS

The Jones & Laughlin Steel Corporation's Aliquippa Works operates two tinning lines for the manufacture of tin plate for use in the canning industry. Tin lines, numbered 3 and 4, operate using the proprietary halogen electrolytic tinning processes.(1)(2) The electroplating of tin onto steel strip is shown on Figure 1. One side of the strip is tinned by

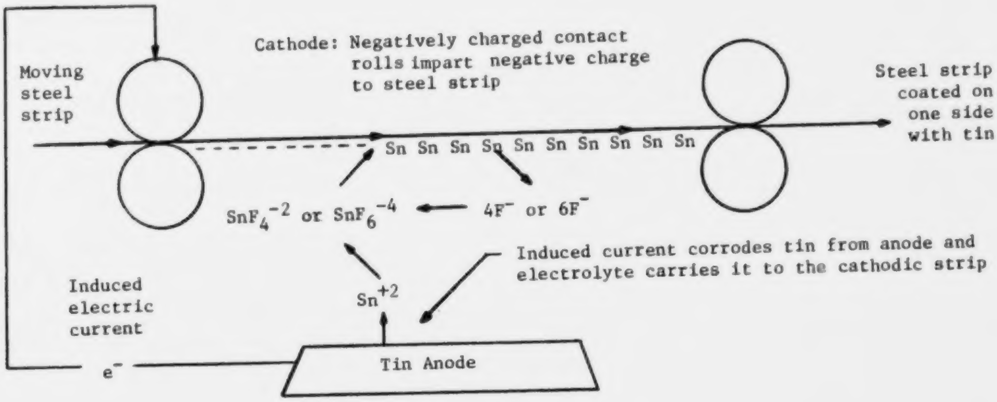

Cathode: Negatively charged contact rolls impart negative charge to steel strip
Moving steel strip
Steel strip coated on one side with tin
Sn Sn Sn Sn Sn Sn Sn Sn Sn Sn
SnF_4^{-2} or SnF_6^{-4}
$4F^-$ or $6F^-$
Induced current corrodes tin from anode and electrolyte carries it to the cathodic strip
Induced electric current
Sn^{+2}
e^-
Tin Anode

Figure 1. The Halogen Electrolytic Tinning Process

rolling the strip into an electroplating bath which has solid tin bars or anodes submerged at the bottom of the bath. The composition of the bath and an induced electric current allow the tin to corrode from the anode and deposit on the steel strip cathode in a thickness dictated by the amount of electric current and the speed of the steel strip.

In addition to tin and fluoride, sodium chloride, chelating and brightening agents, and hydrochloric acid are required in the bath for proper electrodeposition, but the economic consequence of their use is small compared to the use of tin and fluoride.

At various locations along the plating bath, usually near a contact roll, the strip tends to rise to the surface, making it susceptible to drying. To prevent drying a water hose is mounted over the strip and applied as needed. This practice not only serves as a deterrent to strip drying, but indirectly is a make-up for water leakage and evaporative losses.

WASTEWATER CHARACTERIZATION

The electrolyte solution is rinsed from the strip in the recovery rinse tank after plating. The recovery rinse tank is an immersion rinse to which deionized water is continuously added. Figure 2 shows this rinse.

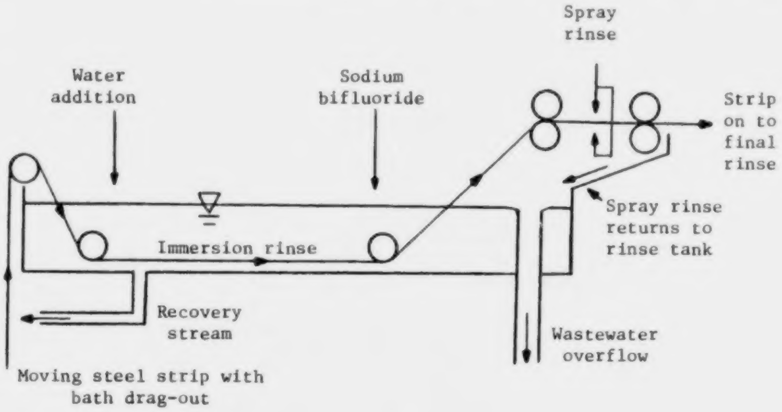


Figure 2. The Recovery Rinse Tank

The recovery rinse is so named because the intent of this rinse is to recover plating chemicals by rerouting a portion of this rinse back to the plating bath. The point at which the recovery water is returned to the bath is on one side of the strip as it leaves the bath. This serves to rinse some of the electrolyte from the strip, resulting in less "drag out" from the tinning bath. Also, dry sodium bifluoride salt is added to the recovery rinse tank. This material is added on an as-needed basis by operators to prevent the recovery tank solution from becoming milky, a phenomenon associated with a defective product. It is thought that the cause of this phenomenon is a precipitation reaction resulting from a deficiency of fluoride in the recovery tank. After the strip emerges from the recovery tank, a spray rinse is applied which drains back into the recovery tank.

EXPERIMENTAL APPROACH

Out of all of the mass inputs into the recovery tank, only a small portion is recovered in the recovery stream. Most of the tin and fluoride that exit this immersion rinse are discharged in wastewater streams. The recovery tank overflow contains over 95% of the tin, fluoride and other electrolyte chemicals contained in rinsewaters.

In order to obtain a statistically adequate data base, a continuous flow recording device and a time actuated composite sampler were used to characterize the overflow from the #3 line recovery tank over a total of 160 hours of operation. The results showed that the recovery tank overflow averaged 59 ± 16 gallons per minute. The tin content was calculated to be 320 ± 99 milligrams per liter. Fluoride was 1426 ± 783 milligrams per liter. These concentrations represent average mass rates of 226 pounds per day and 1010 pounds per day for tin and fluoride, respectively. It was also observed that tin and fluoride concentrations in the recovery tank overflow varied inversely with overflow rate. It is inferred from this observation that the overflow rate (or water use rate) is an operator controlled variable that affects tin, fluoride and water losses. Continuous chart recordings of the overflow rate indicate that short and long term flow variations are caused by three major factors. These factors are:

(A) Line speed; As strip passes through the recovery tank, the strip's shear force on the tank water tends to increase the depth of the discharge side of the tank causing a greater overflow. This does not occur, however, on #4 Tin Line which incorporates a "surge line" to convey rinsewater back to the entry end of the tank.
(B) Hot deionized water pressure; Depending on the level of activity of other associated Tin Plate Department operations, line pressure at the discharge points of spray rinses can vary by as much as 100 percent. Since there are no flow controls (or automatic pressure controlling devices) on any of the rinsing operations, flow rates will vary as a function of line pressure.
(C) Different operators will adjust throttling valves on rinsewater lines as perceived necessary for adequate rinsing.

All three of these factors indicate that the use of water for rinsing is dictated by physical consequences and not necessarily by the solubility and chemical characteristics that normally should be used to prescribe a rinsing program. It is presumed that with a conscientiously applied program of rinsewater use, the average amount of rinsewater required would be somewhat lower than that level found in the characterization survey.

Other significant losses of tin and fluoride are housekeeping losses, such as leakage and spillage collected in the basement sump under each tin line. These losses were found to contain an average of 96 lbs./day of tin and 126 lbs./day of fluoride for each tin line.

The summary of the sampling survey indicates that from 115,500 to

201,750 lbs. of tin are discharged each year from both tin lines in rinsewaters, leakage and spillage. The volume flow which carries this tin ranges from 150 to 190 gallons per minute during operations. This flow also carries from 328,750 to 510,000 lbs. per year of fluoride.

A RINSING MODEL

In order to effectively understand the rinsewater system, as well as predicted cause/effect relationships within the system, a mathematical model based on material balance considerations was developed.

MODEL ASSUMPTIONS

The basis for the model development is shown in Figure 3.

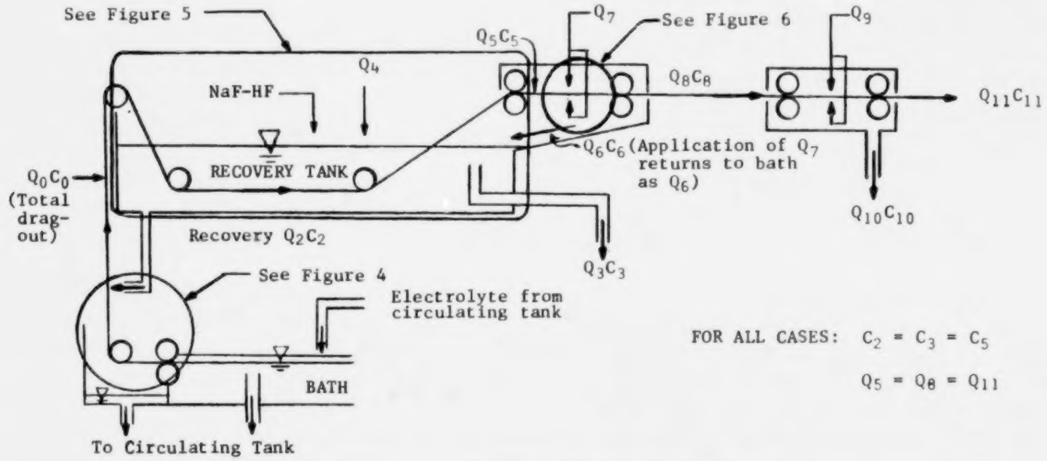

See Figure 5
Q_5C_5
Q_7
See Figure 6
Q_9
Q_4
NaF-HF
Q_8C_8
$Q_{11}C_{11}$
Q_6C_6 (Application of Q_7 returns to bath as Q_6)
Q_0C_0 (Total drag-out)
RECOVERY TANK
Recovery Q_2C_2
Q_3C_3
$Q_{10}C_{10}$
See Figure 4
Electrolyte from circulating tank
FOR ALL CASES: $C_2 = C_3 = C_5$
$Q_5 = Q_8 = Q_{11}$
BATH
To Circulating Tank

Figure 3. Tin Line Rinsing Schematic For Mass Balance Claculations

Before the mathematics of the rinsing process can be developed, certain assumptions must be made. These include:

(A) Finite Volume: The strip carries with it (at a certain line speed) a finite coating of fluid whenever it leaves a bath or spray.
(B) Continuity: The electrolytic chemical concentration of the finite coating is the same as that of the bath in which it was immersed. In the case of a spray rinse, the rinsewater completely mixes with the finite coating to form a coating of different concentration.
(C) Wringer Efficiency: All of the wringer rolls between rinses will be assumed to have the same efficiency. This implies as in Figure 3 that $Q_5 = Q_8 = Q_{11}$. (In reality, these are all different at different times depending on operator adjustment and frequency of maintenance replacement of the wringer rolls).
(D) No Evaporation: It will be assumed that between the bath and Q_{11} there is no significant evaporation.
(E) Uniformity: The tin and fluoride concentrations throughout the recovery rinse tank are uniform, i.e., $C_1 = C_2 = C_5 = C_3$. (The strip averages almost

1100 feet per minute through the tank, and observed eddy currents caused by the strip's shear force serve to strengthen this assumption.)

(F) Fixed Recovery: The rate of recovery water which is sprayed on the strip as it leaves the bath will be fixed at 3 gallons per minute (average of field measurements).

(G) Assumed and Measured Values: Using values found in the characterization survey and operating parameters the concentrations and flow that will be used in the development of this model are in Table 1.

TABLE 1. VALUES USED IN MODEL DEVELOPMENT

Recovery tank tin concentration	-	320 mg/l
Recovery tank fluoride concentration	-	1426 mg/l
Recovery tank overflow	-	59 gal./min.
Recovery tin concentration	-	17 gm/l
Bath fluoride concentration	-	35 gm/l

(H) Constant Constituent Ratio: For any concentration of tin in the recovery rinse, the ratio of fluoride to tin must remain greater than or equal to (1426 mg/l F)/(320 mg/l Sn) = 4.46. (This is an assumption based upon the necessity of sodium bifluoride additions to the recovery tank.)

(I) Steady State: The tin line has no line stoppages, and a steady state condition of operation is experienced. This steady state condition also implies that the line speed is constant and directly proportional to the dragout.

MODEL THEORY

To formulate a model to describe this rinsing operation, it is necessary to state all of the known relationships for each individual application of rinsewater. In each of these relationships, there are known and unknown quantities. Through algebraic manipulation among the relationships the unknown quantities can be narrowed down to several solvable quadratic equations. To begin the modeling, the tin dragout from the bath will be quantified. A simplified portion of Figure 3 is shown in Figure 4 as the location where the strip leaves the plating bath and is sprayed on one side with recovery water.

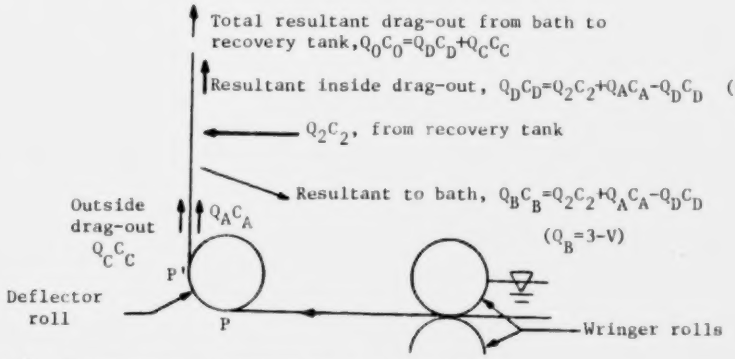

Total resultant drag-out from bath to recovery tank, $Q_0C_0=Q_DC_D+Q_CC_C$
Resultant inside drag-out, $Q_DC_D=Q_2C_2+Q_AC_A-Q_DC_D$ $(Q_D=Q_A+V)$
Q_2C_2, from recovery tank
Resultant to bath, $Q_BC_B=Q_2C_2+Q_AC_A-Q_DC_D$
$(Q_B=3-V)$
Outside drag-out Q_CC_C
Q_AC_A
P'
P
Deflector roll
Wringer rolls

Figure 4. Recovery Rinsewater Application.

Since the deflector roll is grooved and serves merely to change the direction of the strip, it will be assumed that $Q_C = Q_A$, i.e., both sides of the strip have equal volumes of water per lineal foot. (Although the deflector roll does "wring" the strip to a certain extent, it will be assumed that during the movement between P and P', some liquid is lost tangentially from the outside of the strip, balancing the amounts on both sides at point P'.) Also, it will be assumed that out of the 3 gpm, Q_2, that is sprayed on the strip, only a certain volume, V, stays on the strip. The fraction of Q_2 that flows back to the plating bath, Q_B, equals (3-V). In addition the total volume of liquid on the inside of the strip (after the application of Q_2), Q_D, is the sum of V and Q_A. In summary the volumes of Q_D and Q_B can be represented as

$$Q_D = Q_A + V \text{ and } Q_B = 3-V \qquad (1a),(1b)$$

In order to quantify the total dragout from the bath, $Q_0\ C_0$, refer to Figure 3 and note:

$$Q_0\ C_0 = Q_2\ C_2 + Q_3\ C_3 \qquad (2)$$

which is actually a rough mass balance around the recovery tank. This equation excludes the quantity $Q_6\ C_6$ on the left side of the equation and $Q_5\ C_5$ on the right side. These terms can be considered equal if the dragout from the recovery tank is assumed negligible. Substituting known values for Q_2, C_2, Q_3 and C_3:

$$Q_0\ C_0 = 19840^{*} \qquad (3)$$

$Q_0\ C_0$ can also be represented exactly by

$$Q_0\ C_0 = Q_C\ C_C + Q_D\ C_D \qquad (4)$$

which is the summation of the dragout on both sides of the strip after the application of Q_2. Substituting values from equation (3) and from Table 1, equation (4) becomes

$$19840 = 17{,}000\ Q_C + Q_D\ C_D \qquad (5)$$

Referring again to Figure 4, the complete mass balance of the spraying of recovery water can be represented as

$$Q_2\ C_2 + Q_A\ C_A = Q_B\ C_B + Q_D\ C_D \qquad (6)$$

Substitution of known values from Table 1 and equations (1a) and (1b), and using $C_D = C_B$ (Assumption B) yields

$$960 = 17{,}000\ Q_A = (3-V)C_B + (Q_A + V)C_B \qquad (7)$$

---

* Units for C_X and Q_X are mg/l and gpm respectively, but will be excluded for ease of mathematical manipulation.

Similar substitutions into equation (5) and recalling that $Q_A = Q_C$ yields

$$19840 = 17{,}000\, Q_A + (Q_A + V)C_B \tag{8}$$

Equations (7) and (8) can be combined to form the quadratic equation

$$Q_A^2 + .945Q_A + .50_AV + .028V = 1.751 = 0 \tag{9}$$

which has the solutions $Q_A = .71$ gpm, $V = 1.5$ gpm when equations (1), (2), (3), and (4) are used as constraints. Substituting these values into equation (1) yields $Q_D = 2.21$ gpm and $Q_B = 1.5$ gpm. Also $Q_C = Q_A = .71$ gpm. Making similar substitutions into equation (4) yields $C_D = 3512$ mg/l.

The exact mass balance around the recovery tank can be represented [as compared to equation (2)] as

$$Q_C\, C_C + Q_D\, C_D + Q_4\, C_4 + Q_6\, C_6 = Q_2\, C_2 + Q_3\, C_3 + Q_5\, C_5 \tag{10}$$

This mass balance is illustrated in Figure 5.

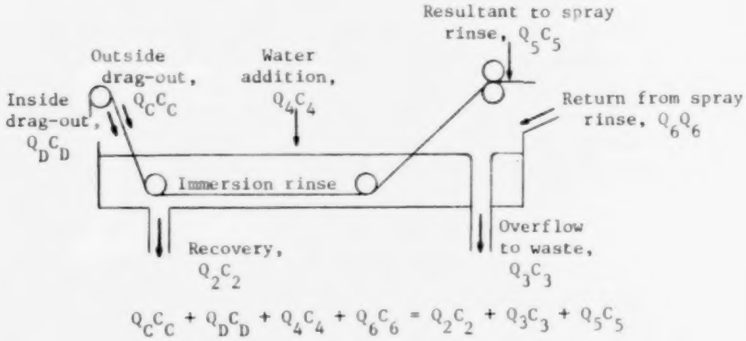

Resultant to spray rinse, Q_5C_5
Outside drag-out, Q_CC_C
Water addition, Q_4C_4
Inside drag-out, Q_DC_D
Return from spray rinse, Q_6Q_6
Immersion rinse
Recovery, Q_2C_2
Overflow to waste, Q_3C_3
$Q_CC_C + Q_DC_D + Q_4C_4 + Q_6C_6 = Q_2C_2 + Q_3C_3 + Q_5C_5$

Figure 5. Mass Balance In Equation (10)

Making all known substitutions into equation (10) and using $Q_6 = Q_7 = 20$ gpm (from field measurements) reduces (10) to the two variable equation

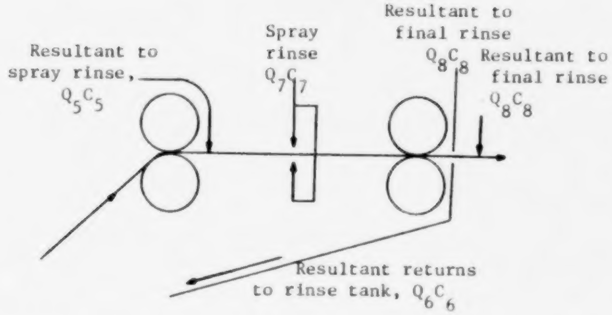
$$Q_6 = (3200_5 + 8.48)/20 \tag{11}$$

Also, the complete mix of the next rinse that drains back into the recovery tank can be represented as

$$Q_5\, C_5 + Q_7\, C_7 = Q_6\, C_6 + Q_8\, C_8 \tag{12}$$

This mass balance represented by equation (12) is illustrated in Figure 6. Using assumptions B and C, $Q_5 = Q_8$ and $C_8 = C_6$, and substituting in to equation (12) reduces to the two variable equation

$$3200_5 - 20C_6 = C_6\, Q_5 \tag{13}$$


Resultant to spray rinse, Q_5C_5
Spray rinse Q_7C_7
Resultant to final rinse Q_8C_8
Resultant to final rinse Q_8C_8
Resultant returns to rinse tank, Q_6C_6

$$Q_5C_5 + Q_7C_7 = Q_6C_6 + Q_8C_8$$

Figure 6. Mass Balance in Equation (12)

Equations (11) and (13) can be combined to form

$$Q_5^2 + .0265Q_5 - .5300 = 0 \qquad (14)$$

which has the solution $Q_5 = .71$. Substitution of this result in (11) yields $C_6 = 11.8$ mg/1. Finally using $Q_9 = 30$ gpm obtained from field measurements in the final rinse complete mix produces $C_{10} = C_{11} = .27$ mg/1. This result indicates that essentially no aqueous tin remains on the strip after the last rinse. A similar analysis can be used to calculate fluoride flows around the recovery. All results are summarized in a mass balance illustrated in Figure 7.

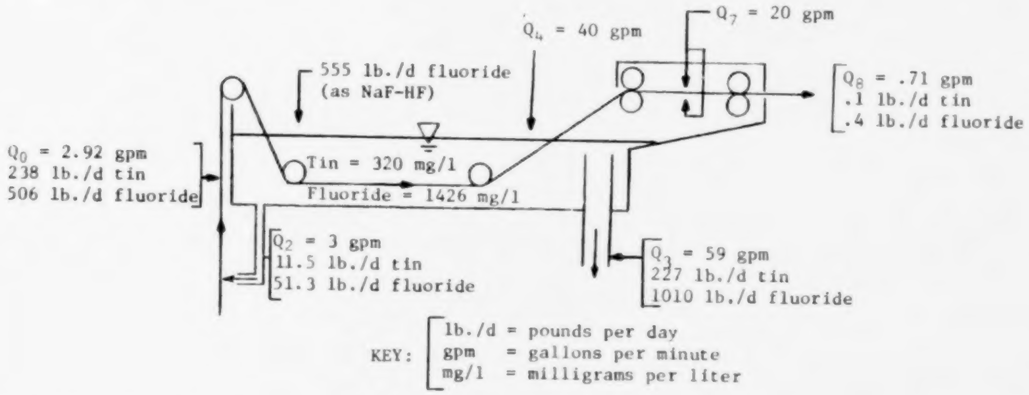

Q_7 = 20 gpm
Q_4 = 40 gpm
555 lb./d fluoride (as NaF-HF)
Q_8 = .71 gpm
.1 lb./d tin
.4 lb./d fluoride
Q_0 = 2.92 gpm
238 lb./d tin
506 lb./d fluoride
Tin = 320 mg/1
Fluoride = 1426 mg/1
Q_2 = 3 gpm
11.5 lb./d tin
51.3 lb./d fluoride
Q_3 = 59 gpm
227 lb./d tin
1010 lb./d fluoride
KEY:
lb./d = pounds per day
gpm = gallons per minute
mg/1 = milligrams per liter

Figure 7. Mass Balance of the Recovery Tank Using the Model.

USE OF THE MODEL FOR IN-PLANT WATER RECOVERY

Using the framework presented by the model theory, it is possible to project the effects of measured charges in rinsing practices. Any rinsing change discussed, here, is presumed to have a beneficial effect on the overall tin and fluoride mass balances, i.e., changes that result in less tin and fluoride being wasted to treatment via rinsewaters.

One simple change in operating practice is to use recovery tank water, instead of fresh water, for strip wetting in the plating bath. This reduces the use of fresh water and allows for re-use of rinsewater.

Another means of increasing recovery (or reducing waste) is to use the mass balance model to prescribe a change in the rinsing program. As shown in Figure 7, the amounts of tin and fluoride recovered is limited, because the recovery flow cannot exceed 3 gpm. Thus, the only other way to increase recovery is to increase the concentrations in the recovery tank. This increase in concentration can be effected by reducing the volume of water used in the recovery rinse. As shown in Figure 7, Q_4 and Q_7 are the only sources of fresh water input, and either can be reduced to raise the recovery tank concentrations.

Both Q_4 and Q_7 are used to dilute the rinse tank, but Q_7 has the added purpose of a spray rinse. This use of Q_7 is an example of counter-current rinsing, which is described in various literature as a more efficient use of water than any once-through use. (3)(4) Thus, Q_4 should be eliminated and any deficiency caused by its elimination can be made up using Q_7. This allows Q_7 to be the single control parameter which can be used to regulate recovery tank concentration and overflow rate.

The overflow rate, Q_3, is the dependent variable used to represent the effects of varying Q_7, since it contains the mass rate Q_3C_3, the most significant loss of tin and fluoride from the system. Thus Q_3 is used as the indicator of net effects of changes made on the rinsing system.

This analysis will proceed with the intention of representing the recovery tank concentration as a function of the recovery tank overflow, Q_3. To begin, the mass balance around the recovery tank [equation (10)] will be examined. From Figure 5,

$$Q_C\ C_C + Q_D\ C_D + Q_6\ C_6 + Q_4\ C_4 = Q_2\ C_2 + Q_3\ C_3 + Q_5\ C_5 \qquad (10)$$

The values C_D, Q_6, C_6, C_2, C_3, C_5 and Q_3 will vary as the inflow to recovery tank is changed. The values C_2, C_3 and C_5 are all equal and will be considered simply as C, the recovery tank concentration. The values Q_C, C_C, Q_5 are known from the model development. $Q_4 = 0$ and is eliminated. Therefore, the unknown values in this equation are C_D, Q_6 C_6, Q_3 and C.

The value C_D can be simplified using equation (6), and recalling that $C_D = C_B$

$$C_D = \frac{Q_2\ C + Q_A\ C_A}{Q_B + Q_D} \qquad (15)$$

All of the values in equation (15) are known, except C.
The value Q_6 can be reduced by using the volume balance around the recovery tank.

$$Q_C + Q_D + Q_4 + Q_6 = Q_2 + Q_3 + Q_5 \qquad (16)$$

Substituting all known values reduces this equation to

$$Q_6 = Q_3 + .79 \qquad (17)$$

Also the complete mix of the application of Q_7 [equation (12)] reduces to

$$C_6 = \frac{Q_5\ C_5}{Q_6 + Q_8} \quad \text{(where } C_7 = 0,\ C_7Q_7 = 0\text{)} \qquad (18)$$

Substituting equation (17) into (18) with other known values reduces to

$$C_6 = \frac{.71C}{Q_3 + 1.5} \qquad (19)$$

Substituting equations (15), (17), and (19) into equation (10) produces

$$Q_C\ C_C + Q_D\ \frac{Q_2C + Q_A\ C_A}{Q_B + Q_D} + (Q_3 + .79)\ \frac{.71C}{Q_3 + 1.5} = C(Q_3 + Q_2 + Q_5) \qquad (20)$$

Substituting all known values into equation (20) yields

$$C = \frac{19260Q_3 + 28890}{Q_3{}^2 + 2.71Q_3 + 2.32} \qquad (21)$$

This function is plotted in Figure 8. Also in Figure 8 is the prediction for fluoride using the constituent ratio assumption.

The projections in Figure 8 should be considered only as physical mass balance functions which were calculated without considering product quality. Any recovery tank concentration that results in greater masses of tin and fluoride on the strip as it leaves the application of Q_7, will require greater amounts of rinsewater in the final rinse, Q_9. This necessity may outweigh the benefits of the higher recovery tank concentration. Also, the fluoride to tin ratio of 4.46 is an assumption based on sampling results. At this writing there is no known equilibrium relationship between tin and fluoride in the recovery tank. In actuality, this ratio may change as the concentration of tin and fluoride change.

TESTING THE MODEL

In order to evaluate the performance of the rinsing model, a test was conducted whereby in-plant flows of rinsewater were reduced to increase the recovery tank concentrations. Over a period of three weeks the use of rinsewater was systematically reduced so that the overflow from the recovery tank was lowered to less than 20 gallons per minute. Also accomplished was the use of 2 gpm of recovery tank water for strip wetting. Results of this testing are illustrated in Figure 9.

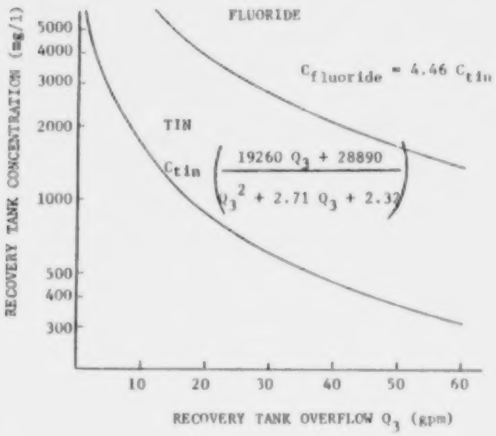


Figure 8. Rinsing Model Recovery Tank Concentration Vs. Overflow Rate

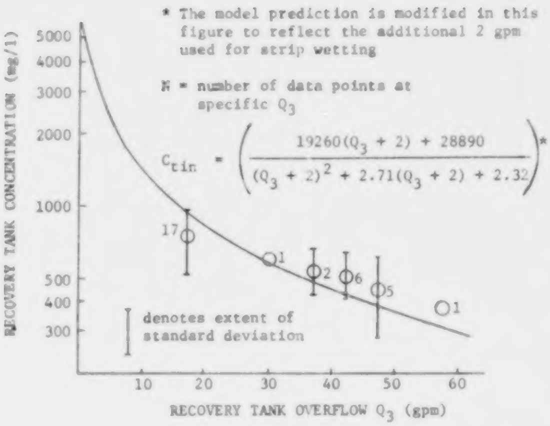


Figure 9. Results of Model Testing

The data points for tin follow the general path of the predicted model. Fluoride analyses remained statistically unchanged and therefore were excluded from further analysis. Testing below a Q_3 of 17 gpm was prohibited by physical constraints associated with the rinsing tank. (7)

Although the model predictions for tin were not followed exactly and although fluoride modeling was excluded for further analysis, the desired trend of reducing mass rates of discharges was followed Using the beginning and endpoints in Figure 9 it can be calculated that a 40% reduction in tin mass rate via Q_3 was achieved. Since the fluoride concentration remained unchanged, it was calculated that a 70% reduction in fluoride mass rate, via Q_3, was achieved due simply to a reduction in the flow rate of Q_3. These reductions do not represent those possible. Further testing, at Q_3 less than 17 gpm, could be performed if the physical limitations preventing this were eliminated. These limitations could be eliminated by a rinsewater control system which maximizes recovery and minimizes losses.

A MODIFIED RINSING MODEL

Assuming that an engineered set of rinsing controls are installed at the J&L operation and that the functional relationship of the model is accurate, a new mass flow condition is constructed to represent steady state rinsing. Two extremes of this steady state rinsing model can be constructed. Phase I represents steady state at $Q_3 = 17$ gpm, the endpoint of the model test. The mass balance associated with Phase I is shown in Figure 10. Also shown in Figure 10 are the conditions of steady state Phase II which represent the ultimate endpoint of $Q_3 = 0$. (The flow rates in parentheses are the average daily flow rates assuming a 12% delay rate. Without parentheses is flow during operation, i.e., during delays flows are off.) Phase II may not be amenable to a quality product, and is only an extrapolation used for comparison purposes.

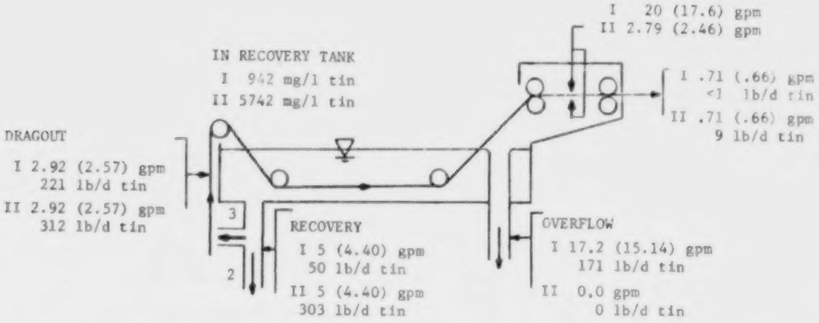

I 20 (17.6) gpm
II 2.79 (2.46) gpm
IN RECOVERY TANK
I 942 mg/l tin
II 5742 mg/l tin
I .71 (.66) gpm
<1 lb/d tin
II .71 (.66) gpm
9 lb/d tin
DRAGOUT
I 2.92 (2.57) gpm
221 lb/d tin
II 2.92 (2.57) gpm
312 lb/d tin
3
2
RECOVERY
I 5 (4.40) gpm
50 lb/d tin
II 5 (4.40) gpm
303 lb/d tin
OVERFLOW
I 17.2 (15.14) gpm
171 lb/d tin
II 0.0 gpm
0 lb/d tin

Figure 10. The Modified Mass Balance

RECOVERY ANALYSIS USING THE MODIFIED MODEL

There are several recovery technologies which can be used to recover tin (and in some cases, fluoride) from process wastewater. These technologies include electrolytic recovery, chemical precipitation, evaporation, electrodialysis and reverse osmosis. (3)(4)(5)(6) The mass rates in Figure 10 can be scaled up to reflect both of J&L's tin lines' wastewater, including leakage and spillage, and all of the wastewaters generated in each of the Phases can be applied to each of the technologies.(7) A comparative summary of these applications is in Table 2.

TABLE 2. COMPARISON OF THE MODIFIED RINSING MODEL APPLIED TO RECOVERY ALTERNATIVES

	(Cost Unit/Year)			
Alternative	Net Value Of* Recovered Tin	Cost Of** Alternative	Net Value*** Of Alternative	Rank
Phase I & Electrolytic Recovery*****	11.4	4.2	7.2	2
Phase II & Electrolytic Recovery*****	18.3	4.2	14.1	1
Phase I & Electrodialysis	11.4	6.0	5.4	4
Phase II & Electrodialysis	8.4	2.9	5.5	3
Phase I & Reverse Osmosis****	11.4	7.3	4.1	6
Phase II & Reverse Osmosis****	8.4	3.8	4.6	5
Phase I & Chemical Precipitation	5.3	4.2	1.1	8
Phase II & Chemical Precipitation	5.6	2.7	2.9	7
Phase I & Evaporation	11.5	23.4	-11.9	10
Phase II & Evaporation	8.3	11.1	-2.8	9
No Recovery	-12.9	0	-12.9	11

* This value is calculated as AB-CD where: A is the amount of tin recovered; B is the unit value of recovered tin (different for different recovery methods); C is the amount of tin lost to wastewater; and D is a reasonable value of the lost tin.

** Capital recovery and operation.

*** Net value of recovered tin minus cost of alternative.

**** Reverse osmosis may not be a viable alternative because the process has not been tried in this application.

***** Electrolytic recovery is not associated with the tin plating production facility, but is a separate treatment method that uses similar electrochemical principles.

Electrolytic recovery is shown to have the best economic potential. This is due to the fact that recovered tin can be recycled directly in a tin smelter with no intermediate refining steps. Electrodialysis and reverse osmosis are somewhat lesser economic choices, but are still better than the "No Recovery" option. Chemical precipitation has a lesser benefit because the tin would have to be extracted from a hydroxide sludge. Evaporation is not attractive in this application due to high capital and energy costs associated with this option. In each case, the Phase II application has a higher economic benefit compared to the Phase I application, and economic recoveries can be interpolated for rinsewater reductions between the values defined by these two extremes.

CONCLUSIONS AND RECOMMENDATIONS

(1) A model for tin line wastewater application was developed, tested and shown to be a useful representation of the rinsing system.

(2) Although J&L can continue to produce a high quality tin plating effluent from the Chemical Rinse Treatment Plant that will meet all applicable regulations, there appears to be several tin recovery alternatives that are economically favorable.

(3) This study has shown that a more careful application of rinsewater can reduce the mass rates of tin and fluoride discharge and it is recommended that improvements to the rinsing system continue.

(4) The requirements and effects of fluoride were not adequately represented by this study, and it is recommended that a better understanding of the disposition of fluoride be pursued.

(5) It is recommended that a wastewater monitoring program be instituted for a better understanding of rinsing requirements.

(6) It is recommended that a training program for associated operating personnel be developed, which would include operating parameters to be maintained and goals which stress maximization of recovery and minimization of waste.

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INVESTIGATION OF THE SOLID-LIQUID PHASE SEPARATION OF PREHEATED AND PIPELINE CHARGED COKE BATTERY CHARGING LIQUOR

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ABSTRACT

Inland's preheat and pipeline charged "C" Battery was built with a solid-liquid phase separation system containing a series of tanks to separate the coal fines collected during the charging process from the charging liquor. This phase separation system did not remove enough coal fines to prevent plugging of the charging liquor spray nozzles and a build up of material in the charging main when the liquor was recycled. Consequently, several phase separation methods were investigated on the laboratory, pilot plant, and plant scale to establish their ability to decrease the solids content of the "C" Battery charging liquor to a concentration suitable for recycling. These methods were: gravity settling, horizontal belt filtration with and without precoat, hydrocyclone separation, spiral rake classification, conventional flotation, and dissolved air flotation.

All of the phase separation methods were able to separate coal fines to some degree, but three methods, namely, gravity settling, dissolved air flotation, and horizontal belt filtration with precoat gave the best results. Gravity settling is easy to operate, but requires a large amount of land area for installation of a pit and the use of chemical additives to accelerate the settling of fines. Dissolved air flotation requires chemical additives and a liquor with a high solids content for best operation. Horizontal belt filtration requires a precoat for efficient operation. In view of the variable solids and tar concentrations in the charging liquor, the gravity settling method was selected and settling pits were installed to separate coal fines from charging liquor at Inland's "C" and No. 11 preheated and pipeline charged coke batteries.

INTRODUCTION

In 1974 and 1978, Inland Steel commenced operation of "C" Battery(1) and No. 11 Battery(2), respectively. Both batteries are equipped with coal preheating and pipeline charging systems(3). In this system, wet coal is preheated by hot gases to 220-260°C(2-4) to remove moisture from the coal prior to charging. The preheated coal is conveyed into the ovens by steam in two pipelines. Coal fines are carried into the charging main during oven charging where they are removed by recycled charging liquor sprays. The liquor is diverted to the coal fines recovery system where it is cleaned of solids and recycled. However, during the initial phase of "C" Battery's operation, the coal fines recovery system did not function efficiently and large amounts of coal fines in the recycled charging liquor caused plugging of the spray nozzles in the charging main. Therefore, a study was initiated to investigate methods to improve the solid-liquid phase separation in the coal fines recovery system.

In this paper, the testing of various devices on the laboratory, pilot plant, and plant scale are discussed in terms of improvement in the solid-liquid phase separation of the "C" Battery charging liquor. On the basis of this investigation, conclusions were drawn concerning the phase separation devices tested, which led to the selection of the most plausible phase separation method - the gravity settling pit. The performance of the plant scale settling pit operation was evaluated.

LITERATURE REVIEW

In comparison to conventional wet charged coke batteries, preheated coke batteries can utilize relatively high percentages of weakly coking coals in the blend, and reduce airborne particulate emissions.(4) However, the capture of these particulates by various liquor streams has transformed air pollution into a water based environmental problem.

Because the technology of utilizing a preheated and pipeline charged coke battery for manufacturing blast furnace coke is relatively new, the literature on the solid-liquid phase separation for charging liquor from these batteries is rather limited. There appears to be only two literature sources on this subject - the British Carbonization Reserach Association (BCRA)(5-8) and Degremont-Laing.(9)

The BCRA work on the phase separation of charging liquor included pilot scale testing of several mechanical phase separation devices in a combined flowsheet which consisted of a decantation tank, froth flotation cells, and rotary vacuum disc filter. In the test, the final filter cake product contained less than 50% solids. The filtrate was reported to be essentially free of solids, although no quantitative data on solids concentration was reported.(5,6) The presence of tar and fine coal particulates in the charging liquor coupled with variable and low solids concentration, appeared to affect the separation efficiency and the operation of the various phase separation devices. For example, it was reported that blinding of the filter fabric occurred in the filter unit when the charging liquor contained an appreciable amount of tar.

Another solid-liquid phase separation approach investigated by BCRA involved increasing the tar concentration of the charging liquor to 15-25% (dry basis) by remaining on the "charging main" cycle for an extended period, instead of switching to the "collecting main" cycle soon after charging. Under these conditions, it was found that the continuous pusher type centrifuge (Alfa-Laval Company) gave excellent results (i.e., high throughput rate and a dry product with 10-15% moisture) provided the charging liquor was thickened by a preconcentration step (sink/float separation or flocculation-decantation step) and the liquor tar concentration was 15% or less.(7,8) In addition, another dewatering device, called a squeezor, was tried on prethickened charging liquor. Cationic and anionic polyelectrolytes were first added to flocculate the thickened slurry, then it passed into a drainage section over a filtering belt, and finally the sludge entered a pressing section where air at a pressure of up to 70 kPa was applied to both sides of the filter cloth to squeeze the sludge. A solid material containing about 20% moisture was produced at the rate of about 3.3 kg/m^2 s dry solids. The cake thickness varied from 4 to 7 mm. The squeezor type filter press was tested in collaboration with Degremont-Laing. The squeezor press appeared to perform well even with the addition of preheater washer fines to the charging liquor. It was also indicated that the dry solid product from the squeezor press was recycled at the rate of 2% of the preheater throughput rate.(8)

The Degremont-Laing(9) phase separation system for the charging liquor included: (1) a fines wetting tank for the addition of two chemicals, ferrous sulfate and a polymer, and (2) a slurry sedimentation tank. An additional stage of prolonged heating of the slurry was necessary when the tar content of the slurry exceeded 10%. The cleaned liquor was of such a quality that it could be recycled in the charging main; however, the solids concentration of the treated clean liquor was not specified. The initial solids content of the charging liquor was reported to be 3000-4000 mg/kg, and the size consist was about 80% -0.15 mm. It was stated that the phase separation system should process liquor at a temperature high enough to keep the tar in a fluid stage. In addition, the flow of liquor should be by gravity in order to minimize pumping requirements and pump related problems, and the collection of the concentrated slurry at the clarifier underflow should be as straight forward as possible. Operating data for a commercial Degremont-Laing charging liquor phase separation system was not reported.(9)

This literature review includes information on the solid-liquid phase separation of charging liquor published after the experimental test program was planned.

EXPERIMENTAL TEST PROGRAM

The solid-liquid phase separation of preheated and pipeline charged "C" Battery charging liquor was investigated by the following methods:

LABORATORY SCALE

- Jar test
- Leaf filtration

PILOT PLANT SCALE

- Horizontal belt filter test with and without precoat
- Hydrocyclone test
- Spiral rake classifier test
- Conventional froth flotation test

Dissolved air flotation test

PLANT SCALE

Conical Tank Test

EXPERIMENTAL PROCEDURE AND EQUIPMENT

The plant scale conical tank test with the charging liquor was conducted before any of the other tests. Modifications made to the original conical tank system affected all the laboratory and pilot scale tests and, therefore, the conical tank test is discussed first. "C" Battery was converted from side charging to top charging in an attempt to reduce the amount of solids going to the coal fines recovery system. During side charging, coal enters the oven at an angle from the pusher side of the oven. Under top charging, coal enters the oven from the top through one of the decarbonization holes. The plant scale conical tank test was made only during side charging conditions, whereas most other phase separation tests were conducted under both side and top charging conditions at "C" Battery.

PLANT SCALE TEST

Conical Tank

In the original design of the coal fines recovery system, the charging liquor containing coal fines, tar, and other compounds (Table I) flowed by gravity from the charging main to a conical tank for solid-liquid separation. Later, a vertical and a horizontal tank were added to the system in series to improve the solid-liquid phase separation of the conical tank underflow, but the additional tanks did not solve the problem of recycled fines. The flow diagram of the original charging liquor system is given in Figure 1. A 1/10 scale model of the original conical tank was built in order to determine the mechanism of the solid-liquid separation. Subsequently, an aeration ring and two whirljet nozzles were placed in the conical tank in order to introduce fine uniformly distributed air bubbles which float the coal fines to the top of the tank. Based on the phase separation tests with the model conical tank, two Heyl and Patterson nozzles were placed in the conical section of the existing tank at "C" Battery. The modified conical tank, which has about 20,000 dm^3 liquor capacity, is shown in Figure 2.(10)

LABORATORY TESTS

Jar Test

In order to determine the feasibility of using gravity settling for separating coal fines from charging liquor, laboratory jar tests were performed. These tests were conducted in 500 ml and 1000 ml jars to determine the optimum dosage and synergistic effect of cationic and anionic polymers on the settling rate of coal fines in the charging liquor. Two liquor samples from the conical tank intake and the horizontal tank (Figure 1) were tested at a temperature of about 60 $^\circ$C. Betz Cationic 3390 and Betz Anionic 3330, as well as Nalco Cationic 7763 and Nalco Anionic 7132 polymers, were used. The

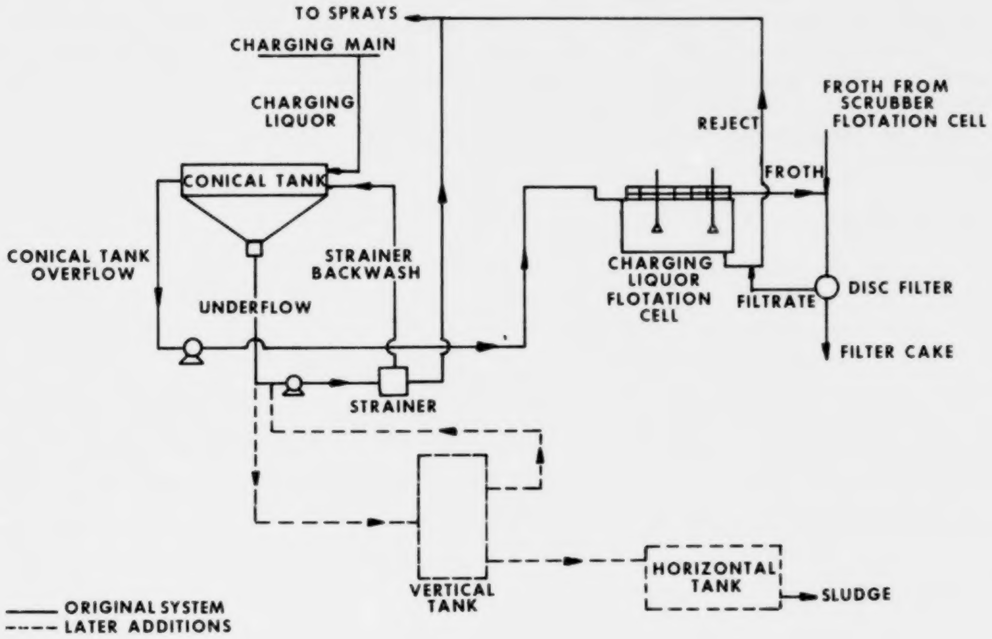
TO SPRAYS
CHARGING MAIN
CHARGING LIQUOR
CONICAL TANK
CONICAL TANK OVERFLOW
UNDERFLOW
STRAINER BACKWASH
STRAINER
REJECT
FROTH FROM SCRUBBER FLOTATION CELL
FROTH
CHARGING LIQUOR FLOTATION CELL
FILTRATE
DISC FILTER
FILTER CAKE
VERTICAL TANK
HORIZONTAL TANK
SLUDGE
ORIGINAL SYSTEM
LATER ADDITIONS

Figure 1 Schematic Flow Diagram of the Original Charging Liquor System at C Battery

TABLE I

TYPICAL CHEMICAL ANALYSIS OF CHARGING LIQUOR

Solids (%)	
Fixed Carbon	62.10
Volatile Matter	32.40
Ash	5.50
Sulfur	0.85
Oil & Tar (Chloroform Solubles)	7.66
Energy	30 MJ/kg
Liquid (mg/kg)	
Free Ammonia (as N_2)	250
Fixed Ammonia (as N_2)	2950
Phenol	540
Cyanide	11
Thiocyanate	550
Sulfate	950
Sulfide	12
Oil	60
Chlorides	9725
Suspended Solids	2000
Total Dissolved Solids	15448
pH (units)	8.6

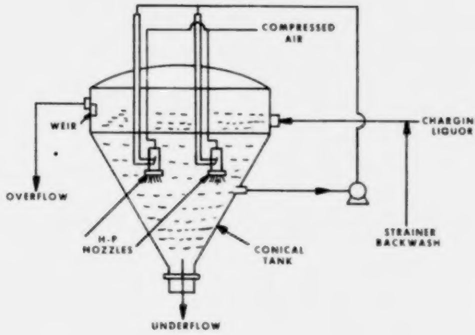
COMPRESSED AIR
WEIR
OVERFLOW
CHARGING LIQUOR
H-P NOZZLES
CONICAL TANK
STRAINER BACKWASH
UNDERFLOW

Figure 2 Modified Conical Tank with Heyl and Patterson Nozzles $^{(10)}$

cationic polymer dosage ranged from 5 to 45 mg/kg, whereas, 0.25 to 10 mg/kg of anionic polymer was used. The cationic polymer was first added to the liquor with rapid mixing for 60 seconds followed by the addition of the anionic polymer and mixing for another 30 seconds. The settling rate was determined by observing the solid-liquid interface as a function of time. Samples of the supernatant liquor were taken to determine the solids concentration.

Leaf Filtration

A 108 mm diameter EIMCO leaf filter with a filter area of $0.00929 m^2$ was employed to evaluate filter cloths and to study the filtration characteristics of "C" Battery charging liquor at 25°C to 90°C. Three filter cloths, nylon (NY-518F), polyethylene (PO-801HF), and polypropylene (POPR-853F), were tested. Approximately $3.79 dm^3$ of charging liquor was filtered using a vacuum pump with a suction capacity of 101.3 kPa. The filter time, suction, and filtrate volume were recorded, and the wet and dry weights of the cake were determined.

PILOT SCALE TESTS

Horizontal Belt Filter

An Eimco Model 112 horizontal belt filter was used to separate the solids from the charging liquor. The belt filter was 3.7 m long by 0.3 m wide, had the abililty to generate a suction of 6.2 kPa and ran at a speed of 0.043 m/s. Two different filter cloths were used during the testing program, nylon (NY-518F) and polypropylene (POPR-853F). The nylon cloth had finer pores than the polypropylene cloth. Liquor was fed from various sources to the unit through a feed box at a rate of 0.63 to 3.15 dm^3/s. The liquor was pulled through the filter belt into a drain trough with a suction that was usually 5.0 kPa, but always greater than 2.5 kPa. The solids formed a cake and remained on the belt until it reached the end, where the cake fell onto a conveyor. Samples were taken of the feed, filtrate, and filter cake from the unit for solids content analyses.

Horizontal Belt Filter with Precoat

In order to increase the filtration efficiency of the horizontal belt filter and overcome the problem of filter cloth plugging due to the tar content of the charging liquor, a precoat filtration system was employed. The same Eimco horizontal belt filter was used for the precoat filtration study. The belt filter ran at a speed of 0.03 m/s for all tests. Two different filter cloths were used during the pre-coat filtration runs; nylon (NY-518F), and polypropylene (POPR-853F). The froth from the scrubber flotation cell was fed to the belt filter as a precoating material, since the solids concentration is higher and the tar content is lower. The charging liquor was fed onto the filter cake which was previously formed on the belt. The flow of preheater scrubber effluent varied from 0.21 to 3.79 dm^3/s, whereas, the charging liquor flow rate varied from 0.16 to 1.89 dm^3/s. The belt was maintained at a suction which was usually about 5.0 kPa, but always greater than 2.5 kPa. Samples of charging liquor feed, scrubber liquor feed, filtrate and filter cake were taken for solids content analyses.

Hydrocyclones

Two WEMCO cyclones, 76.2 mm and 152.4 mm in diameter, were employed in the solid-liquid phase separation test of C Battery charging liquor. Two cyclone products were produced in these tests; the cyclone overflow liquor containing mostly -0.045 mm coal particles, and the cyclone underflow liquor which contains coarser coal particles.

The 76.2 mm diameter cyclone had three apexes with diameters of 6.35 mm, 9.5 mm, and 12.7 mm. Feed rates of 0.88, 1.32, and 1.7 dm^3/s were obtained by operating the 76.2 mm cyclone at an inlet pressure of 69, 138, and 207 kPa, respectively. An overflow/underflow volume ratio in the range of 2:1 to 10:1 was obtained by changing the inlet cyclone pressure or the apex diameter.

The 152.4 mm diameter WEMCO cyclone was lined with nitrile rubber in order to prevent corrosion and erosion by materials contained in the charging liquor. This cyclone contained a 50.8 mm diameter hydraulically adjustable hinged apex operating at pressures up to 621 kPa. Tests were made at apex diameters of 15.9 mm, 25.4 mm, 38.1 mm, and 50.8 mm. At operating cyclone inlet pressures of 69, 138, and 207 kPa, corresponding feed rates of 7.26, 11.36, and 13.25 dm^3/s were obtained. An overflow/underflow volume ratio of 10:1 was observed with the 152.4 mm diameter cyclone having an apex of 38.1 mm. The phase separation tests were made using the 152.4 mm diameter cyclone only under top charging conditions.

The cyclone feed, overflow and underflow liquor streams were sampled for suspended solids. The flow rates of the cyclone streams were measured.

Spiral Rake Classifier

A 0.46 m diameter x 3.5 m long spiral SM classifier was employed in the phase separation tests. This WEMCO 150 Series classifier had a full flare tank and a rated capacity of 44.3 dm^3/s for 0.15 mm separation of solid particles as a classifier sand. The rotation of the spiral rakes was set at 0.12 rev/s. The flow rate of the charging liquor feed ranged from 1.89 to 4.40 dm^3/s. Coal solids must accumulate in the bottom of the tank and underneath the spiral rake housing tank before a steady state condition is reached and classified sand is produced. Two classifier products, a classifier sand and an overflow liquor, were sampled along with classifier liquor feed and analyzed for solids concentration.

Conventional Flotation Cell

A 227.4 dm^3 capacity Heyl and Patterson (H+P) flotation cell was used in separating solids as a froth from the charging liquor. The flotation cell operates at a feed rate of 1.20 to 1.89 dm^3/s which gives a retention time of 2 to 3 minutes. One third of the liquor by volume is recirculated at an agitation pressure of 13.5 kPa. Air bubbles are generated when the recycled liquor comes in contact with a curtain of air in the 6 vortex chambers. The fine air bubbles are attached to the solids which carry them to the top of the cell in the form of a froth. Each vortex chamber is equipped with a 9.5 mm diameter ceramic spray nozzle. An air pressure of 34.5 kPa is required to maintain a desired air/liquid flow ratio of 3.74.

Samples of froth, underflow, and feed were taken for solids concentration analyses. The H+P flotation tests were made with and without the addition of 200 mg/kg of alum (aluminum sulfate) as a flocculation agent.

Dissolved Air Flotation Unit

A Carborundum Model 50 Dissolved Air Flotation Unit (DAF) was employed for separation tests with the charging liquor. The DAF unit had a surface area of 2.63 m^2, a 4410 dm^3 flotation tank, and a flow capacity of 3.78 dm^3/s; all tests were performed at 3.78 dm^3/s. The charging liquor enters the unit through a mixing tank into which flocculants can be added. The liquor flows through a pump where air is injected, and into a tank which is pressurized to between 138 and 276 kPa; most tests were performed at 138 kPa. Under pressure, the air dissolves, and, upon release of the pressure in the flotation tank, micron size bubbles are formed which are enveloped by the suspended solids in the charging liquor. These air bubbles contain coal fines and rise to the surface where they are removed as froth by skimmers. Any large particles which settle to the bottom of the tank are removed by a scraper arm. The clean liquor exits through side ports.

Alum and an anionic polymer (Carborundum CF500A) were used separately and together as flocculating agents. The alum and polymer concentrations were 178 mg/kg and 4 mg/kg, respectively. The DAF tests were made only under top charging conditions. Samples were taken of the froth, feed, and underflow from the unit for solids concentration analyses.

RESULTS AND DISCUSSION

The chemical analyses of a typical charging liquor and the contained solids are presented in Table I. The liquor is hot with a temperature of about 90°C. The solids concentration was variable, fluctuating from 400 to 20,000 mg/kg. The solids are high and variable in oil and tar (3-10%). The typical size analysis of the solids indicated that solids containing relatively coarse coal particles are obtained in the charging liquor during side charging than top charging (Table II). The difference in the size of the charging liquor solids may affect the separation efficiency of phase separation devices tested under both charging conditions. The apparent size of the solids may be coarser because of agglomeration of fines that may occur during transport. The agglomeration of coal fines also depends upon the initial solids concentration, and oil and tar concentration, which are known to fluctuate during the charging cycle. Thus, variable solids concentration and the tar content of the solids could have affected the performance of the various phase separation devices that were tested in this investigation.(5-8)

TABLE II

TYPICAL SIZE ANALYSIS OF CHARGING LIQUOR COAL FINES

Screen Size (mm)	Cumulative Weight % Passing C Battery (Side Charging)
"As is" Coal Fines	
0.150	30
0.075	ND
0.045	0.6
0.038	ND

Chloroform Washed Coal Fines*	C Battery (Top Charging)
0.150	72
0.075	58
0.045	43
0.038	39
0.020	30
0.010	16

ND: Not Determined

* Oil and tar free coal fines

Wet Screening done above .038 mm; Coulter Counter Analysis for -0.038 mm fines.

TABLE III

EFFECT OF AIR NOZZLES ON THE CONICAL TANK SEPARATION EFFICIENCY

	Average Solids concentration $\bar{x} \pm \sigma$ (mg/kg)			
No. of Nozzles* in the Conical Tank	Charging Liquor Feed	Strainer Backwash Feed	Underflow from Conical Tank	Solids Removal Efficiency (%) ± σ
0	6273 ± 1582	731 ± 697	5526 ± 956	28 ± 6.6
2	2761 ± 1421	354 ± 228	987 ± 704	71 ± 13.1

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*Heyl and Patterson Nozzles

PLANT SCALE TEST

Conical Tank

Solids concentration in the feed to the conical tank fluctuated during the charging cycle. Typically, there were 400 mg/kg of solids in the charging liquor at the beginning of the side charging cycle. A peak value in the range of 19500 mg/kg was reached approximately 5 minutes into the cycle. In some cases, a second peak was observed.

Based on a constant "C" Battery charging liquor flow rate of 113.6 dm^3/s and an average charging cycle of 11 minutes, the total coal fines carryover during side charging for four oven charges were calculated to be 323, 463, 480, and 654 kg/charge, far greater than the design capacity of 45 to 91 kg/charge. Coal fines carryover increased as much as 50% when two oven charges overlapped. The solids removal efficiency was increased from 28% to 71% when fine air bubbles were introduced in the modified conical tank(10) (Table III and Figure 2). Even with the improved solids-liquid separation efficiency, the solids concentration of the conical tank underflow was still well over 200 mg/kg, the desired level for recycling.

It appears that possible oxidation of the coal particles and changes in the surface characteristics of the coal particles due to tar and oil in the charging liquor may have caused many coal particles to sink rather than float in the conical tank.

LABORATORY TESTS

Jar Test

The results of the laboratory jar tests indicated that a combination of cationic and anionic polymer addition gave the best settling rate of the coal fines in the liquor. Betz polymers gave an equivalent settling rate of about 150 mm/min of coal fines at lower polymer concentrations as compared with Nalco polymers (Table IV). The clear liquor, after the settling of flocculated coal fines for less than 3 minutes, averaged less than 10 mg/kg of suspended solids, thereby suggesting that the settling of coal fines in a pit is a satisfactory method for obtaining a clean charging liquor for recycling to the charging main.

Leaf Filtration

The leaf filtration tests with "C" Battery charging liquor were performed to determine the filterability of the liquor. The results are summarized in Table V. A solids removal efficiency of up to 99.9% was achieved. The clean liquor averaged less than 50 mg/kg of suspended solids. The filtration rate increased with the initial suspended solids concentration in the liquor. The usage of chemical additives did not increase the filtration rate. The Nylon filter cloth NY-518F and the polypropylene cloth POPR-853F appeared to withstand the attack of the various coal chemicals contained in the charging liquor, whereas the polyethylene cloth PO-801HF hardened after filtration.

TABLE IV

LABORATORY JAR TESTS FOR C BATTERY CHARGING LIQUOR

Polymer Combination and Dosage Rate for Settling of Coal Fines*

A. Charging Liquor from the Conical Tank Inlet

	Betz		Nalco	
	Type	mg/kg	Type	mg/kg
Cationic Polymer	3390	20	7763	40
+				
Anionic Polymer	3330	0.5	7132	6

B. Charging Liquor from Vertical Tank Underflow

	Betz		Nalco	
	Type	mg/kg	Type	mg/kg
Cationic Polymer	3390	20	7763	20
+				
Anionic Polymer	3330	0.25	7132	2

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*Equivalent settling rate of about 150 mm/min.

TABLE V

LABORATORY LEAF FILTRATION OF CHARGING LIQUOR

Filter Cloth	Liquor Temp. (°C)	Filtering Vacuum (kPa)	Solids Concentration* (mg/kg)	Moisture In Filter Cake (%)	Solids Removal Efficiency (%)	Filtration Rate ($kg/m^2 \cdot s$)
Side Charging						
NY-518F	25	88	3506	32	99.4	0.03
	25	95	6077	42	99.0	0.11
	25(a)	95	3313	46	99.9	0.05
	25(b)	95	3329	71	98.9	0.06
	44	70	5028	39	99.2	0.05
	70	88	5753	32	99.0	0.08
	80	95	16517	41	97.4	0.26
	80(a)	91	14565	40	97.6	0.23
	80(b)	88	11286	57	97.4	0.19
POPR-853F	25	85	6024	44	98.8	0.02
	25	88	1321	63	99.9	0.07
Top Charging						
NY-518F	25	95	853	44	99.9	0.01

(a) Betz polymer added.
(b) Nalco polymer added.
* Charging liquor

Filtration rates of 0.05 to 0.2 kg/m^2 s were obtained. The suction during the test ranged from 70 to 95 kPa. The filtration of "C" Battery charging liquor was sensitive to the presence of tar and the solids concentration.

A preconcentration step may be required to obtain a feed with a uniform solids concentration in excess of 1000 mg/kg, which is needed for proper unit operation, so that the tar in the liquor does not blind the pores of the cloth.(5,6) The blinding is a result of (1) the absorption of tar on the particle surfaces of coal, and (2) the formation of a sticky thin film of tarry material on the cloth.

PILOT SCALE TESTS

Horizontal Belt Filter With or Without Precoat

Typical results of the horizontal belt filter tests conducted at "C" Battery using a nylon filter cloth (NY-518F) are presented in Table VI. It was found that there is no correlation between the solids removal efficiency and solids concentration in the filtrate. However, it was noted that the lower limit of acceptable solids concentration in the feed was about 1000 mg/kg, below which the belt filter solid removal efficiency is drastically reduced (Figure 3). Thus, the horizontal belt filter appears to be able to clean charging liquor to recyclable levels (less than 200 mg/kg solids concentration) when the solids concentration in the feed is high.

Horizontal belt filter tests with a precoat of the concentrated scrubber effluent indicated a strong correlation between the feed rate and filtration rate of solids (Figure 4). The test data on precoat belt filter operation showed that the solids concentration of the scrubber effluent and the charging liquor fluctuated from 3721 to 62883 mg/kg and 24 to 5668 mg/kg, respectively. Average solids concentration of the filtrate was 122 mg/kg and ranged from 26 to 315 mg/kg. Average thickness of the filter cake was 6.6 mm. The average filter cake moisture content was 29.8% and ranged from 23.0 to 42.7% (Table VI). Precoating the filter cloth with a solid allowed efficient belt filter operation even with charging liquor containing low solids or high tar content. The precoat acts as a porous media which captures fine coal particles and tar present in the charging liquor, and allows the liquor to pass through without blinding the filter cloth.

Hydrocyclones

The tests on the solids-liquid phase separation of charging liquor using the 76.2 mm and 152.4 mm diameter WEMCO cyclones showed that typically during side charging conditions, the 76.2 mm cyclone was effective in producing an overflow containing 100 to 300 mg/kg of suspended solids. However, under top charging conditions, both cyclones failed to provide an overflow with a concentration of suspended solids below 200 mg/kg. The addition of alum (200 mg/kg) did not aid in the cyclone operation.

As shown in Figure 5, the 76.2 mm cyclone during side charging yielded a 95% solids removal efficiency and a concentration of 65-110 mg/kg solids in

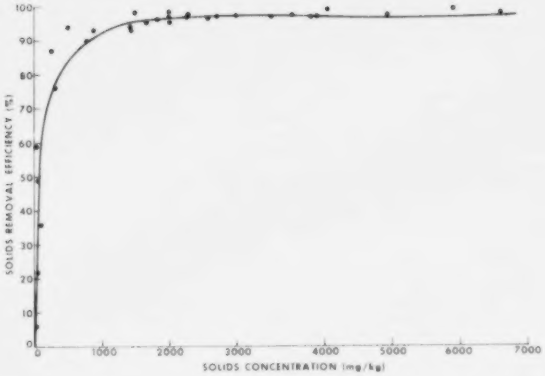

Figure 3 Typical Plot of Solids Removal Efficiency Versus Solids Concentration in the Feed for the Horizontal Belt Filter

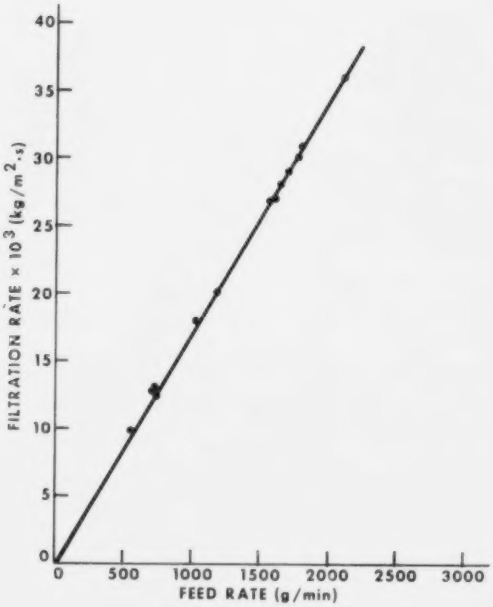

Figure 4 Filtration Rate Versus Feed Rate of Solids in the Combined Charging Liquor and Precoat Scrubber Effluent

TABLE VI

TYPICAL HORIZONTAL BELT FILTER OPERATING DATA FOR CHARGING LIQUOR

Filter Cloth	Average Charging Liquor Solids Conc. (mg/kg ± σ) Feed	Filtrate	Average Filter Cake Moisture (% ± σ)	Solids Removal Efficiency (%)	Filtration Rate (kg/m^2· s)	Average Scrubber Effluent Solids Concentration (mg/kg ± σ)
Side Charging and No Precoat						
NY-518F	973 ± 1535	33 ± 19	16 ± 2	96.6	.0007	*
	1966 ± 2714	48 ± 13	20 ± 5	97.6	.0015	*
Top Charging and No Precoat						
NY-518F	2949 ± 2048	82 ± 20	41 ± 10	97.2	.0050	*
Side Charging and with Precoat using Venturi Scrubber Effluent						
NY-518F	1245 ± 1189	124 ± 90	34.8	99.4	0.028	5101 ± 28885
	2015 ± 1804	222 ± 150	42.7	98.4	0.012	34898 ± 16572
	5668 ± 3132	54 ± 21	23.0	99.8	0.036	48693 ± 35633

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*Scrubber effluent was not used as a precoat.

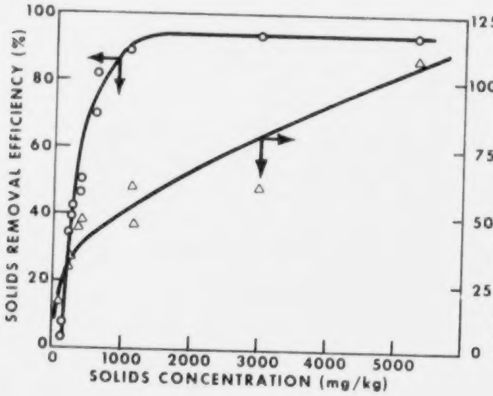

Figure 5 Solids Removal Efficiency and Overflow Solids Concentration Vs Solids Concentration in the Feed for the 76.2 mm Cyclone During Side Charging

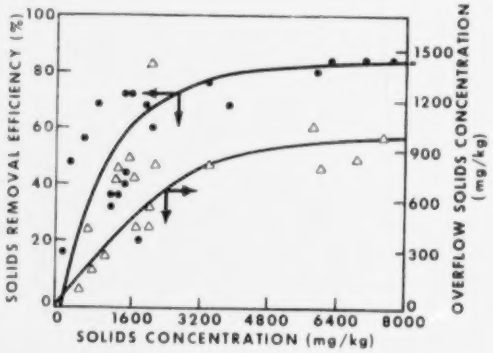

Figure 6 Solids Removal Efficiency and Overflow Solids Concentration Vs Solids Concentration in the Feed for the 76.2 mm Cyclone During Top Charging

the cyclone overflow at a solids concentration in the charging liquor feed above 1500 mg/kg. Under top charging conditions, when over 1500 mg/kg solids are present in the feed, a solids removal efficiency of about 50 to 80% and 500-800 mg/kg of solids concentration in the cyclone overflow were obtained (Figure 6).

The 152.4 mm cyclone tests were conducted only under top charging conditions. During the tests, the solids concentration in the cyclone feed liquor was in the range of 100 to 800 mg/kg. The maximum solids removal efficiency was 50%.

The cyclone size and other related specifications were selected to obtain solids separation at 0.045 mm in the cyclone overflow. The 76.2 mm cyclone gave excellent cleaning when treating charging liquor during side charging conditions. Poor results were obtained with both the 76.2 mm and 152.4 mm cyclones in the phase separation of liquor during top charging conditions. This may be a result of smaller size of the solids contained in the charging liquor during top charging in comparison to side charging (Table II). However, it was very difficult to obtain a true size distribution of solids in the liquor because of agglomeration caused by tar and other surface active substances contained in the charging liquor.

Spiral Rake Classifier

The classifier test data is presented in Table VII. On the average, 55% of the solids in the feed were removed as classifier sand during side charging and 43% during top charging. The solids in the classifier overflow contained 1000 mg/kg, a value much higher than can be recycled to the charging main. The classifier sand had a moisture content of 40 to 50%. The classifier could not by itself clean the liquor, but might be used as a pretreatment system to supply a liquor containing uniform solid concentration to other phase separation devices.

Conventional Flotation Cell

The Heyl and Patterson (H+P) flotation test data obtained during both side and top charging are presented in Table VIII. The underflow from the flotation cell had a moderate solids concentration, except for the test conducted with high tar concentration in the charging liquor and the test when alum was used as an additive. A minimum solids concentration (1000 mg/kg) in the feed is needed before the flotation cell will operate with a high efficiency (Figure 7). The conventional H+P flotation cell operation was not improved with the use of the alum additive and, in fact, alum was detrimental in floating the solids from the liquor. One possible explanation may be the breakage of the alum flocculated particles during the recirculation of about a third of the liquor entering the flotation cell. Poor flotation results could also be obtained in the case of the high tar content liquor, if the tar laden solid particles were too coarse to float and did not have the affinity for the air bubbles required for good flotation response (Figure 7).

TABLE VII

SPIRAL RAKE CLASSIFIER DATA

Solids Concentration (mg/kg ± σ) Feed	Solids Concentration (mg/kg ± σ) Overflow	Moisture in Sand (% ± σ)	Solids Removal Efficiency (%)	Charging Condition
2874 ± 3249	1470 ± 2060	48.5 ± 8.6	55.3	side
1334 ± 1556	1004 ± 1236	40.5 ± 5.8	43.9	top

Feed to the conical tank was the source of the charging liquor used in these tests (Figure 1).

TABLE VIII

CONVENTIONAL FLOTATION CELL OPERATING DATA

Solids Concentration (mg/kg ± σ) Feed	Solids Concentration (mg/kg ± σ) Underlow	Solids Concentration (mg/kg ± σ) Froth	Solids Removal Efficiency (%)	Feed[(1)] Source	Charging Conditions
5932 ± 10098	111 ± 91	1027 ± 11273	84.1	FCT	side
6344 ± 10033(a)	739 ± 412	6944 ± 8310	55.9	FCT	side
1540 ± 295	398 ± 274	16534 ± 14559	73.0	FCT	top
2271 ± 1226(b)	1329 ± 680	10460 ± 20999	49.3	FCT	top
280 ± 470	70 ± 46	269 ± 280	57.5	COF	side
389 ± 454	243 ± 299	829 ± 837	40.0	COF	top
255 ± 277	203 ± 202	2485 ± 4432	46.5	3CO	top

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(1) FCT = Feed to the conical tank
COF = Classifier overflow
3CO = 76.2 mm (3 in) cyclone overflow

(a) Excessive tar in the charging liquor feed
(b) 200 mg/kg alum used as an additive

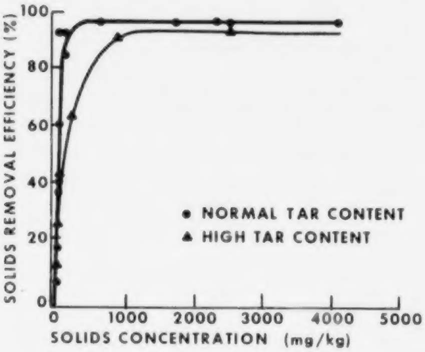

Figure 7 Solids Removal Efficiency Vs Solids Concentration in the Feed for the Conventional Flotation Cell During Side Charging

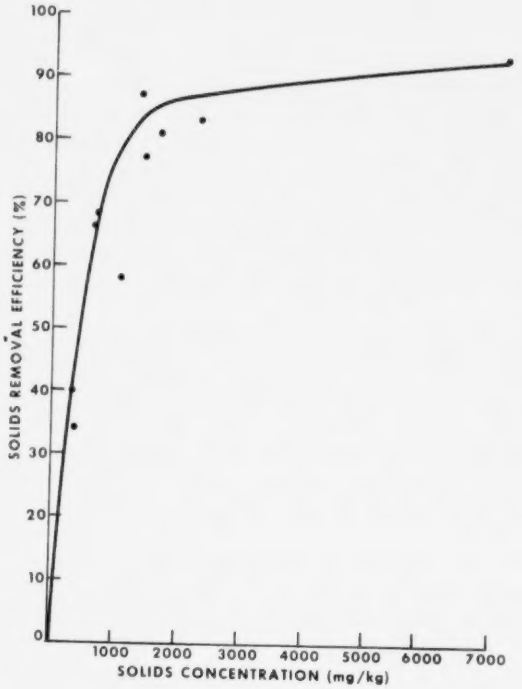

Figure 8 Solids Removal Efficiency Vs Solids Concentration in the Feed for the Dissolved Air Flotation Unit with Alum Addition

TABLE IX

DISSOLVED AIR FLOTATION OPERATING DATA*

Solids Concentration in the feed (mg/kg ± σ)	Solids Concentration in the Underflow (mg/kg ± σ)	Solids Concentration in the Froth (g/kg ± σ)	Chemical Additions
1844 ± 1178	812 ± 723	1277 ± 106	None
2060 ± 3042	257 ± 98	126 ± 89	178 mg/kg alum
631 ± 103	1110 ± 308	51 ± 45	178 mg/kg alum 4 mg/kg polymer
1536 ± 889	1580 ± 507	20 ± 21	178 mg/kg alum 4 mg/kg polymer

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* All samples were taken under top charging conditions.

Dissolved Air Flotation Unit

Three sets of additions were used in testing the dissolved air flotation unit (DAF): no additives, 178 mg/kg alum, and 178 mg/kg alum plus 4 mg/kg anionic polymer. The DAF unit with no additives produced a liquor which averaged 812 mg/kg solids, as compared to 257 and 1374 mg/kg for the liquor when alum and alum plus polymer were added to the system, respectively. Table IX presents the average values for all of the measured parameters. For the DAF tests with no additions, analysis of the percent removal of solids in the feed parameters indicated that there was a lower limit of solids concentration in the feed below which the DAF solids removal efficiency was drastically reduced. No numerical value could be set for the DAF tests with no alum additions due to the small number of experimental data points. For the tests run with alum and alum plus polymer additions, the value of the lower limit was 700 mg/kg and 1200 mg/kg of solids in the feed, respectively. The solids removal efficiency above the limiting point was greater than 85% when alum was added to the system, but only 20% when both alum and polymer were added. The plot of solids removal efficiency versus solids concentration in the feed for the DAF with alum addition is presented in Figure 8.

The DAF operated best at 138 kPa, a value somewhat lower than anticipated from previous work. The reason for this probably is due to the method by which the pressure was increased in the pressurizing tank. This was accomplished by restricting the flow into the flotation chamber. At lower pressures, higher flow rates were permitted. It appears that a high flow rate must be maintained for the DAF unit to function properly. On a full scale unit, higher pressures can be used while maintaining a high liquor flow rate. This increased pressure should enhance the unit's cleaning efficiency and broaden the range of solids concentration that the DAF can efficiently clean.

The DAF produced the lowest solids loading in the clean liquor when alum was added to the system. The alum acted as a flocculating agent which aids in the floating of fine solids. The addition of anionic polymer to the unit offset the effect of the alum addition. Alum is positively charged and the solids in the charging liquor are negatively charged. The alum agglomerates the solids into larger, easier-to-float particles which are still negatively charged. The anionic polymer probably interacts with the agglomerates and disperses them, since both are negatively charged. Large amounts of alum would make the polymer addition useful, but small amounts of additives is the goal in order to be cost effective. A cationic polymer may be of value in flocculating solids, since it would perform in a manner similar to alum and might form even larger agglomerates than alum. Note that alum is beneficial in the DAF but detrimental in conventional flotation.

SETTLING PITS

This investigation has indicated that the following three solid-liquid phase separation methods were superior to the others tested:

1. Gravity settling with polymer addition.
2. Dissolved air flotation with alum addition.
3. Horizontal belt filtration with precoat.

Of the three methods, gravity settling appears suitable for a liquor with widely varying concentrations of solids and tar. Dissolved air flotation functions well for the varying solids loading in the liquor, if the solids content is above 700 mg/kg, but the effect of tar on the unit's operation, maintenance, and cleaning efficiency has not been established. The horizontal belt filter requires a precoat in order to operate efficiently. Both of the latter two require large amounts of maintenance plus operation by skilled personnel. Considering the above factors, and based on the satisfactory operating experience of settling pits of the preheat coke battery at Jones & Laughlin Steel's Aliquippa Works, two settling pits (7.6 x 7.6 x 7.6 m) were installed at Inland's "C" Battery to clean the charging liquor (Figure 9).(4) For the same reason, No. 11 Battery also has two settling pits (9.1 x 9.1 x 7.5 m) to process its charging liquor prior to recycling to the charging main. At any given point in time, only one pit is in operation, and settled coal fines sludge is removed from the other pit by clamshell operation.

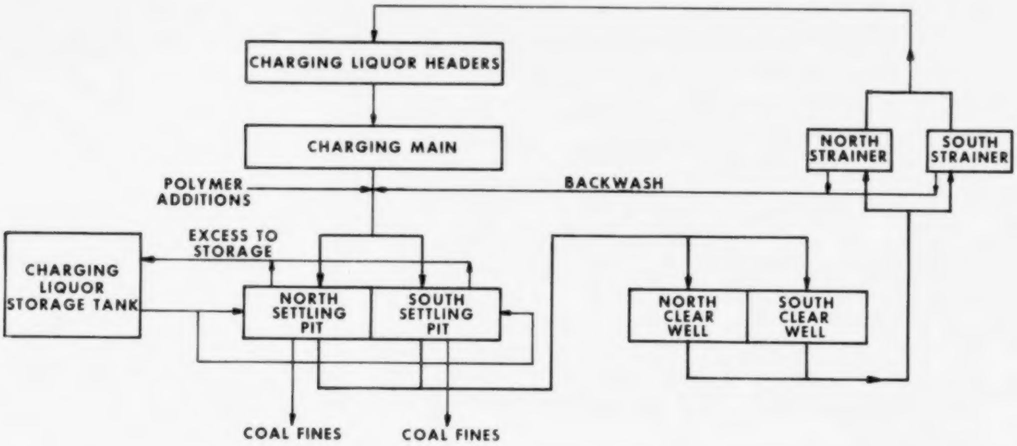
CHARGING LIQUOR HEADERS
CHARGING MAIN
NORTH STRAINER
SOUTH STRAINER
POLYMER ADDITIONS
BACKWASH
EXCESS TO STORAGE
CHARGING LIQUOR STORAGE TANK
NORTH SETTLING PIT
SOUTH SETTLING PIT
NORTH CLEAR WELL
SOUTH CLEAR WELL
COAL FINES
COAL FINES

Figure 9 Schematic Diagram of the Settling Pit Solid-Liquid Phase Separation System (4)

The settling pit operation of the "C" Battery cannot be realistically evaluated at the present time because of the possible presence of some extraneous water flows. Consequently, only the settling pit data for No. 11 Coke Battery will be discussed in some detail.

Based on monthly average data, the clean overflow charging liquor from No. 11 Battery settling pit operation contains as low as 300 mg/kg solids concentration. However, the solids loading in the treated liquor, which is recycled into the charging main, generally fluctuated from 300 - 1000 mg/kg with an average loading of about 600 mg/kg solids. This fluctuation in the solids concentration of the treated liquor might be due to the specific coal blend composition, coal grind, and the type, as well as the dosage, of polymers added to the charging liquor in order to accelerate the settling rate of coal fines in the pit. The retention time of the coal fines in the settling pit was calculated to vary between 20-50 minutes, depending on the level of settled fines in the pit. The polymers used are: Betz Cationic 3390 at 7-10 mg/kg, and Betz Anionic 3325L at 2 mg/kg. It was necessary to use polymers in order to achieve solid-liquid phase separation in the pit. The operating experience indicated that the higher the dosage of the polymer, the lower was the solids loading in the treated recyclable charging liquor.

The coal fines sludge material recovered from the settling pits by a clamshell type operation has a very high moisture content (50-55%), which causes severe handling problems during transport and recycling. This sludge material can be recycled as a boiler fuel in a power station(2,4) or by mixing with coal blends for cokemaking.(8) In order to solve or minimize the handling problem of the settling pit sludge materials, various dewatering methods, such as selective agglomeration of charging liquor coal fines, compacting of the "as is" pit sludge, and the briquetting of pit sludge mixed with other coal fines are currently being investigated.

SUMMARY AND CONCLUSIONS

Various solid-liquid phase separation devices were tested in order to produce a clean recyclable charging liquor at the preheated and pipeline charged "C" Coke Battery. These included: laboratory jar settling tests and leaf filtration tests; pilot scale horizontal belt filter, hydrocyclone, spiral rake classifier, conventional and dissolved air flotation cell tests; and plant scale holding tank and aeration tests. On the basis of the results of this investigation, the following conclusions can be made:

1. The solids concentration of the charging liquor fluctuates during the charging cycle; the tar concentration of the liquor also varies.

2. A minimum solids concentration of about 1000 mg/kg is necessary for an effective solid-liquid separation by the various devices tested, which indicates a need for a preconcentration step.

3. Gravity settling with polymer addition, dissolved air flotation with alum addition, and a horizontal belt filter with precoat gave the best results in achieving high solids removal efficiency (85-95%) and in producing a clean recyclable liquor containing a solids concentration of about 200 mg/kg.

4. In view of the variable solids and tar concentration in the charging liquor, the gravity settling method was selected for solid-liquid phase separation, and settling pits were installed at Inland's "C" and No. 11 Batteries.

5. The processing of charging liquor in the No. 11 Battery settling pits indicated that the settling pit overflow, i.e., the clean recyclable charging liquor, contained a solids concentration as low as 300 mg/kg.

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ASSESSMENT OF THE BIOLOGICAL TREATMENT OF COKE-PLANT WASTEWATERS WITH ADDITION OF POWDERED ACTIVATED CARBON (PAC)

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ABSTRACT

The United States Steel Corporation, in cooperation with the United States Environmental Protection Agency, has conducted an extensive experimental biological-treatment program to develop data relative to Best Available Technology Economically Achievable (BATEA) for coke-plant wastewaters. This program has included testing at both a bench-scale level and a pilot-scale level. One of the features of this program was an assessment of the benefits of addition of powdered activated carbon (PAC) to the biological reactor. In bench-scale reactors gross removal efficiencies, as measured by chemical oxygen demand (COD) and total organic carbon (TOC), were determined with and without PAC. Comparisons were made on the basis of the effects of solids-retention time and on PAC-dose levels. A dual-train pilot-scale study was made at optimum conditions established during the bench-scale research to confirm the bench-scale comparisons. The results indicated that PAC did not significantly enhance effluent quality when compared with the effluent quality of a biological reactor operated at optimum conditions. There was also evidence to indicate that PAC-supplemented biological reactors treating coke-plant wastewater may undergo desorption of a substrate toxic to the thiocyanate-degrading organisms.

INTRODUCTION

Clairton Works of the United States Steel Corporation is one of the world's largest producers of metallurgical coke. In addition, Clairton Works also has a fully integrated system for the recovery and refining of coal chemicals from the coke-oven off-gases. Naturally occurring ammonia is recovered as an anhydrous liquid product through use of U. S. Steel's proprietary PHOSAM* process. Light-oil fractions are separated from the coke-oven gas by a cryogenic-regenerator system, which also yields an ultra-pure, hydrogen-rich gas for consumption in a synthetic-ammonia plant. Complementary systems are operated to recover benzene, toluene, and xylene as well as a complete line of tar-based fractions.

Clairton Works generates somewhat in excess of 9,500 cubic meters per day (m^3/d) [2.5 million gallons per day (MM gpd)] of contaminated water. About 45 percent (%) of this water is generated directly from the coking operation whereas the remaining 55% is attributed to the chemical operations. The typical composition of this contaminated water is shown in Table 1.

The principal elements of the Clairton Works contaminated water treatment facilities are shown schematically in Figure 1. Following gravity separation of both solids and suspended oils in the settling tanks, the contaminated water is processed through the USS CYAM* process also developed by U. S. Steel. Here the water is steam-stripped of so-called "free ammonia", pH-adjusted by the addition of lime to liberate "fixed ammonia", and further steam-stripped to yield a biological plant feed stream of desired ammonia content. In addition to ammonia removal, the CYAM system also removes more than 99% of the free cyanide as well as other acid

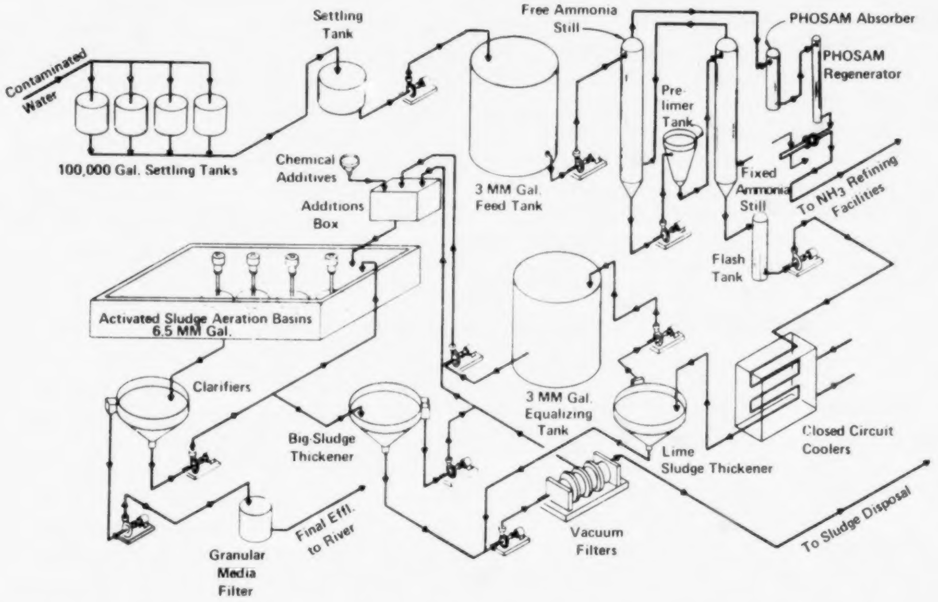
Contaminated Water
100,000 Gal. Settling Tanks
Settling Tank
Free Ammonia Still
PHOSAM Absorber
PHOSAM Regenerator
Pre-limer Tank
Chemical Additives
Additions Box
3 MM Gal. Feed Tank
Fixed Ammonia Still
To NH_3 Refining Facilities
Flash Tank
Activated Sludge Aeration Basins 6.5 MM Gal.
Clarifiers
3 MM Gal. Equalizing Tank
Closed Circuit Coolers
Big Sludge Thickener
Lime Sludge Thickener
Vacuum Filters
To Sludge Disposal
Final Effl. to River
Granular Media Filter

Figure 1. CONTAMINATED-WATER TREATMENT PLANT, CLAIRTON WORKS – UNITED STATES STEEL CORPORATION

gases. Following ammonia removal, the water is cooled and clarified in a conventional center-well, peripheral overflow clarifier prior to biological treatment.

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* PHOSAM and CYAM are trademarks.

The biological-treatment system is a single-stage process consisting of two independent aeration basins operating in parallel. The total system volume is in excess of 25,000 m^3 (6.5 million gallons) with aeration and mixing being provided by low-speed mechanical surface aerators. After biological treatment and clarification, the wastewater passes through dual-media filters before it is discharged into the Monongahela River. The CYAM system and the biological treatment plant have been in operation since 1976.

During the third quarter of 1979, as part of the Mon Valley Consent Decree, the United States Environmental Protection Agency (USEPA) and United States Steel Corporation (USSC) agreed to conduct an extensive experimental program to develop data relative to the application of Best Available Technology Economically Achievable (BATEA) for the Clairton coke-plant wastewaters. Environmental Dynamics Incorporated (EDI) of Greenville, South Carolina was the consultant selected to carry out this program in conjunction with USSC Res[illegible]nd Clairton personnel in cooperation with the USEPA. The program involved extensive testing with bench-scale reactors [0.028 m^3 (7.5 gallons)] and pilot-scale reactors [3.5 m^3 (935 gallons)]. One of the goals of the program was to evaluate the impact of the addition of powdered activated carbon (PAC) to the aeration chamber of a biological system treating coke-plant wastewater. This presentation describes the results of that investigation.

SELECTION OF POWDERED ACTIVATED CARBON

On the basis of previous experience with the use of PAC in petroleum-industry wastewater treatment, EDI selected four commercially available PACs for isotherm testing in order to determine the best PAC for use in the bench- and pilot-scale experiments. The four PACs chosen for isotherm testing on effluent from the Clairton activated-sludge system to determine the absorptivity of the biologically refractory substances in the wastewater were Westvaco Nuchar SA and Nuchar SA-15, and ICI Darco HDC and Darco KB. Because there were no specific, readily measurable substances which could be used as parameters in these isotherm tests, the gross parameters of chemical oxygen demand (COD) and total organic carbon (TOC) were used. In addition, because the wastewater exhibited a high ultraviolet absorbance at 400 nanometers (nm), a normalized absorbance was defined as the ratio of the equilibrium absorbance to the initial absorbance at 400 nm to provide a third isotherm parameter.

Freundlich isotherms[1*] for these three measured parameters are presented in Figures 2, 3, and 4. The COD isotherm (Figure 2) indicated no large difference among the four PACs but showed Nuchar SA-15 marginally better than the other three PACs. Also, the fact that the isotherms were

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* See References.

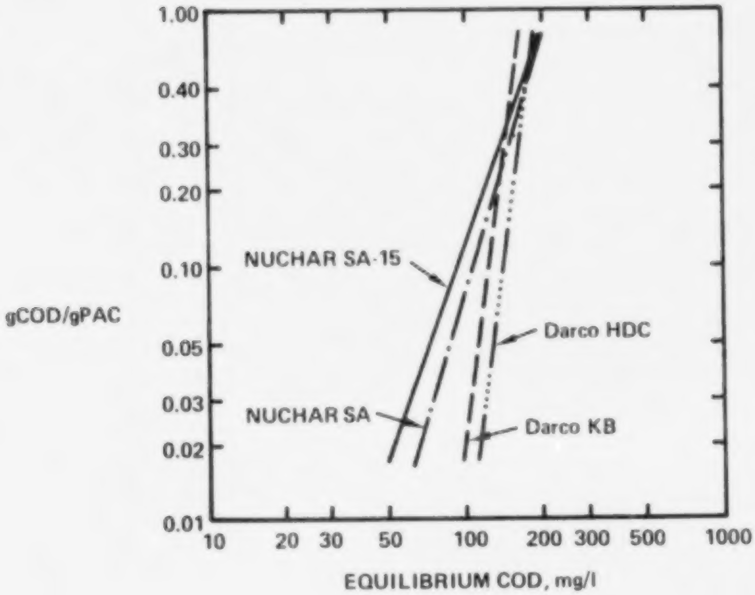

Figure 2. COD ISOTHERMS

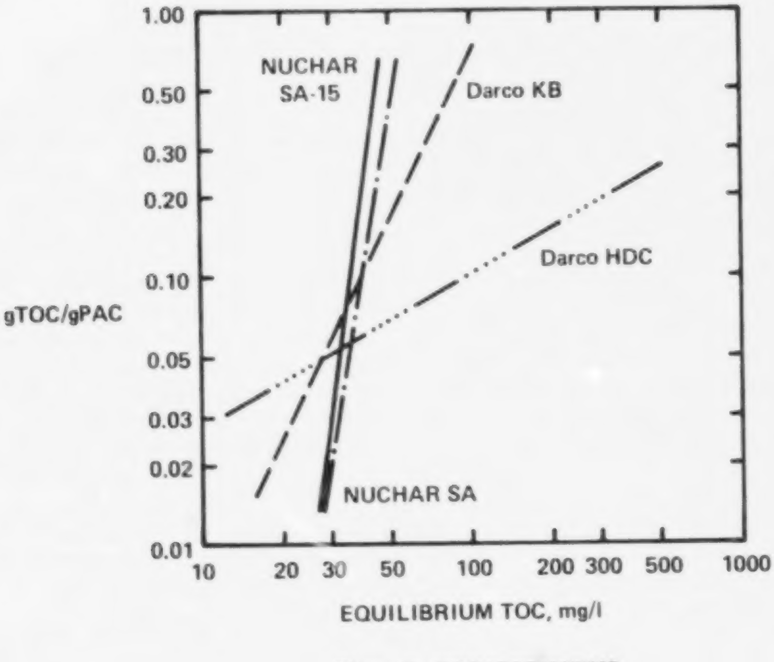

Figure 3. TOC ISOTHERMS

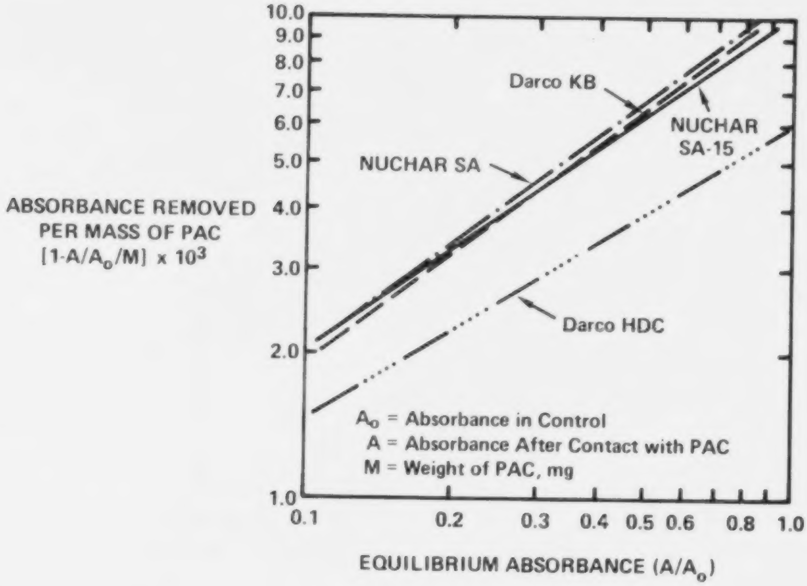

Figure 4. ISOTHERMS BASED ON ULTRAVIOLET ABSORBANCE AT 400 NANOMETERS

nearly vertical was an indication that PAC addition might not significantly enhance the quality of the Clairton wastewater as measured by COD.

The TOC iostherms (Figure 3) showed a somewhat wider variation among the PACs, with the Darco HDC showing the greatest effect on TOC equilibrium with changes in PAC concentration; however, additional TOC reduction, even at the high PAC dosage, was small.

All four PACs gave substantial reductions in the absorbance at 400 nm (Figure 4), indicating a high degree of removal of the substance or substances responsible for this absorbance. No attempt was made to determine these substances or to determine their level of concentration in the wastewater. Therefore, the carbons may have been removing a substance present in only minor concentrations that would not affect biological oxidations. Nuchar SA-15 and Darco HDC were marginally better than Nuchar SA and Darco KD.

On the basis of the three gross parameters tested in these isotherms, Nuchar SA-15 was selected for use in the remainder of the program; however, it was agreed by all concerned with the project that there was very little detectable difference among any of the candidate carbons.

EFFECTS OF PAC ADDITION TO BENCH-SCALE REACTORS

Previous investigations[2,3] have shown that the effectiveness and economic viability of PAC addition for upgrading activated- sludge performance is a function of both carbon-addition rate and solid-retention time (SRT). To explore both effects, carbon doses were varied to provide aeration-basin carbon (Nuchar SA-15) concentrations of 1500, 3000, and 6000 milligram per litre (mg/l) at 20- and 60-day SRTs. Control reactors at 20- and 60-day SRTs without carbon were also maintained. All reactors were fed from the same 0.208 m^3 (55 gallon) drum, which was continuously fed a slipstream from the influent line to the Clairton aeration basin. The water volume was maintained at a constant 0.189 m^3 (50 gallon) by a float and valve mechanism controlling the slipstream flow. The feed drum was also constantly agitated to obtain concentration equilization.

Analytical data for the reactors are presented in Tables 2 and 3. These data represent the average values obtained during the last week of a six-week period of operation. Examination of the data at both a 20-day SRT and a 60-day SRT indicated that better performance was obtained at the 1500 mg/l PAC level than at the higher PAC levels. The only exception to this was sludge- volume index (SVI), which showed better settling characteristics with increasing PAC levels, as would be anticipated. The poor performance of the higher level PAC reactors at both SRTs in terms of COD, TOC, and five-day biochemical oxygen demand (BOD_5) was attributed to the loss of thiocyanate metabolism in these reactors. It was believed that a desorption from the carbon of some substance toxic or inhibitory to the thiocyanate-oxidizing organism had occurred. Such desorption phenomena have been observed in other studies of the application of PAC to industrial wastewaters.[4,5] The loss of thiocyanate metabolism did not occur in either of the non-PAC control reactors, which was taken as an indication that there was no inhibitory level of a toxic substance in the feed at the time the PAC reactors lost thiocyanate metabolism. In PAC units, it is theorized that substances present in the feed at sub-inhibitory concentrations can accumulate on the carbon. If desorption then occurs, the material can be eluted at much higher than normal concentrations, resulting in inhibition of the organisms.

A comparison of performance of the non-PAC reactors with the best PAC reactors (1500 mg/l carbon dose) is presented in Table 4. It was evident that the 60-day SRT non-PAC reactor performed better than the 20-day SRT non-PAC reactor. It was also evident that there was not much improvement in the 1500 mg/l PAC reactor at a 60-day SRT over the 20-day SRT. Overall, it was concluded from the data that there was not sufficient improvement in performance at a 60-day SRT to justify the use of PAC.

The ammonia-removal performance as measured by the specific ammonia-removal rate is presented in Table 5. The data indicate that there was a definite benefit from carbon addition when the reactors were maintained at a 20-day SRT. It should also be noted, however, that there was no apparent additional benefit in the use of higher PAC concentrations at the 20-day SRT. A possible explanation for this was that only a small amount of carbon was required to absorb a low level toxic material inhibitory to nitrification. Thus, no benefit was obtained from the remainder of the carbon that was added. The data at a 60-day SRT indicate that carbon addition was of no benefit with respect to ammonia removal as measured by the specific ammonia-removal rate. Also, the 60-day SRT non-PAC control reactor exhibited better ammonia removal than the 20-day SRT non-PAC control reactor, which would indicate that a 60-day SRT was closer to optimal than a 20-day SRT.

The data presented in Table 6 show the results of the specific organic analysis of the influent and effluents of the reactors by gas chromatographic/mass spectrographic (GC/MS) procedures. Twenty-four hour composites were taken at the conclusion of the bench-scale test for these analyses. The results indicated an excellent reduction of most of the priority pollutants through biological treatment. The results also indicated that carbon addition was of no significant benefit in terms of providing additional reductions in the priority pollutants.

Static bioassays, with PIMEPHALES PROMELAS (fat-head minnows) as test organisms, were performed on the influent and effluents of each reactor at the conclusion of the experimental run. Effluents were collected over a period of 48 hours. The results, presented in Table 7, indicated that PAC was beneficial when the reactors were controlled at a 20-day SRT, with the LC 50 (lethal concentration at which 50 percent of the test organisms die during a 96 hour test) getting higher with increasing levels of PAC to the point where an LC 50 was not reached at 6000 mg/l PAC concentration. However, when the SRT was maintained at 60 days, PAC was of no benefit. The LC 50 results at a PAC level of 3000 and 6000 mg/l at an SRT of 60 days were probably due to the suspected desorption from the carbon that had occurred in these reactors.

EFFECTS OF PAC ADDITION TO A PILOT-SCALE REACTOR

A 20-week pilot study was undertaken at the conclusion of the bench-scale experiments, which consisted of a 9-week acclimation period followed by an 11-week period of intensive testing. Two pilot units were utilized, one serving as a control while the other contained PAC. Each unit consisted of a 3.5 m^3 (935 gallon) aeration chamber separated from an integral clarifier by a sliding baffle. Fine-bubble aeration through dacron-covered diffusers provided mixing and oxygen transfer. Optimum operating conditions, established in the bench-scale studies, were maintained in both units. Each unit was fed influent from a common feed tank, which was supplied by a side stream off the main influent feed line to the Clairton aeration basin. Based on the bench-scale results, an SRT of 60 days was maintained in both reactors and a PAC concentration of 1500 mg/l was maintained in one of the reactors.

The average performance results covering the 11 weeks of intensive testing are presented in Table 8. The results paralleled the bench-scale results in that carbon addition did not measurably improve effluent quality. The only possible exception would be with ammonia-removal performance, where the PAC reactor exhibited a better specific ammonia-removal rate and a lower ammonia-N average effluent concentration, as shown in Table 9. However, as shown in Figure 5, the PAC reactor, near the end of the testing period, lost thiocyanate metabolism, so that the ammonia-N load on the nitrifiers was reduced with the overall result that effluent ammonia-N concentration was lower. The loss of thiocyanate metabolism in the pilot PAC reactor gave additional support to the PAC desorption theory expressed in the discussion of the bench-scale results. One additional

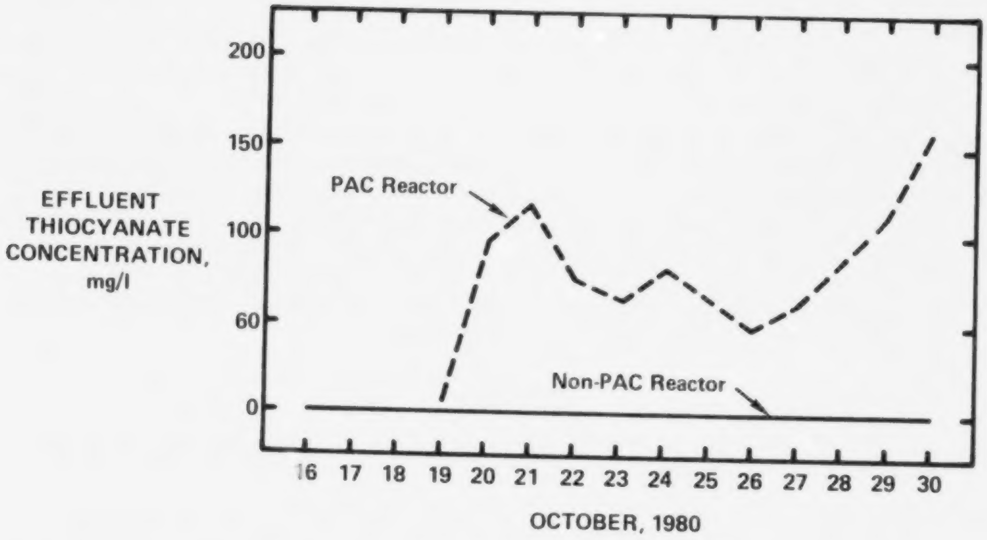

Figure 5. EFFLUENT THIOCYANATE ANALYSIS

result during the desorption incident that was not recognized or noticed in the bench-scale reactors was the tendency for the biomass in the carbon reactor to float and foam. The foam was exceptionally unusual because it would not break up when anti-foam was added. The noncarbon reactor also was susceptible to foaming but it was easily controlled with antifoam. No explanation for this observation has been offered.

During the intensive testing period, four separate composite samples were collected and analyzed for specific organic compounds (priority pollutants) by GC/MS procedures. The results of these analyses are presented in Tables 10, 11, 12, and 13, and showed that effluent from the PAC reactor was no better than effluent from the control reactor. The sample collected October 30, 1980 was particularly noteworthy, however, because it indicated that the PAC reactor effluent had several polynuclear aromatic hydrocarbons in higher concentrations than the influent. This sample was collected after the PAC reactor had lost thiocyanate metabolism from a suspected carbon desorption, which has lead to the speculation that these compounds were the substances desorbed and were the cause of the loss of thiocyanate metabolism.

Two 96-hour flow-through bioassays were performed on the reactor effluents, and the results are presented in Table 14. The first bioassay was made at the mid-point of the testing period, and the second bioassay was made at the end of the testing period. Although an LC 50 was not encountered in the first bioassay, the PAC reactor exhibited less effect on the fat-head minnows than the control. In the second bioassay, the PAC effluent had an LC 50 of 49 percent while the control effluent did not have an LC 50; in fact, only 15 percent of the test minnows were affected by the full-strength water. It was assumed that the poor bioassay test with the PAC effluent was a direct result of the suspected desorption incidents that had previously occurred.

CONCLUSIONS

The effluent from a properly operated and controlled biological reactor treating coke-plant wastewater is not significantly improved by the addition of PAC to the aeration basin of the reactor; in fact, such addition may be detrimental to effluent quality because of the possibility of desorption of toxic substances that affect thiocyanate metabolism. Conversely, the effluent quality of a sub-optimally operated biological reactor treating coke-plant wastewater might be improved by the addition of PAC to the aeration basins, as long as desorption does not occur.

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It is understood that the material in this paper is intended for general information only and should not be used in relation to any specific application without independent examination and verification of its applicability and suitability by professionally qualified personnel. Those making use thereof or relying thereon assume all risk and liability arising from such use or reliance.

Table 1. COMPOSITION OF COKE-PLANT CONTAMINATED WATER

Ammonia -- 1500-2000 PPM

Phenol -- 800-1200 PPM

Thiocyanate -- 600- 700 PPM

Cyanide (Total) -- 200- 400 PPM

Oil/Grease (Freon Extractibles) -- 2000-4000 PPM

Total Suspended Solids -- 300-1500 PPM

pH -- 8-9

Temperature -- 130-170°F.

Table 2. COMPARISON OF PERFORMANCE AT A SOLIDS-RETENTION TIME OF 20 DAYS

Parameter[a] PAC Concentrations	0	1500	3000	6000	Influent[b]
COD	308	219	712	521	2760
TOC	91	43	95	78	817
BOD_5	12	19	86	51	1089
Oil and Grease	2.4	2.1	2.5	2.9	18
Phenol	0.11	0.07	0.07	0.06	562
Thiocyanate	0.22	0.34	320	200	370
Ammonia-N	122	80	2	37	56
MLSS	7852	7108	8751	11698	-
MLVSS	5827	6416	7696	11182	-
MLVSS'[c]	-	4991	4846	5482	-
SVI	42	43	28	19	-

a All values are mg/l unless otherwise stated.

b After 26% dilution with river water.

c Assumes a 95% volatility for PAC.

Table 3. COMPARISON OF PERFORMANCE AT A SOLIDS-RETENTION TIME OF 60 DAYS

Parameter[a] PAC Concentrations	0	1500	3000	6000	Influent[b]
COD	182	170	208	726	2760
TOC	53	50	51	126	817
BOD_5	6	14	19	90	1089
Oil and Grease	2.5	4.7	4.2	4.1	18
Phenol	0.08	0.05	0.07	0.12	562
Thiocyanate	0.13	0.34	2.7	400	370
Ammonia-N	91	122	86	3	56
MLSS	13350	12624	15327	17932	-
MLVSS	11350	11172	14130	16298	
MLVSS'[c]	-	9747	11280	10598	
SVI	66	69	58	30	

a All values are mg/l.
b After 26% dilution with river water.
c Assumes a 95% volatility for PAC.

Table 4. COMPARISON OF PERFORMANCE BETWEEN BEST PAC REACTORS AND NON-PAC REACTORS

Parameter[a]	SRT=20 Days		SRT=60 Days		Influent[b]
PAC Concentrations	0	1500	0	1500	--
COD	308	219	182	170	2760
TOC	91	43	53	50	817
BOD_5	12	19	6	14	1089
Oil and Grease	2.4	2.1	2.5	4.7	18
Phenol	0.11	0.07	0.08	0.05	562
Thiocyanate	0.22	0.34	0.13	0.34	370
Ammonia-N	122	80	91	122	56
SVI	42	43	66	69	--

[a] All values are mg/l.

[b] After 26% dilution with river water.

Table 5. COMPARISON OF AMMONIA-REMOVAL PERFORMANCE

	SRT = 20 Days				
PAC Concentrations[a]	Influent[b]	0	1500	3000	6000
Total Ammonia-N[c] Remaining	145	122	80	79	85
Influent Flow, l/day	-	15.26	15.98	14.54	14.69
MLVSS'[d]	-	5827	4991	4846	5484
Specific Ammonia-Removal Rate x 10^3 $\left(\frac{\text{mg NH}_3\text{-N}}{\text{mg VSS day}}\right)$	-	2.13	7.34	6.99	5.66
		SRT = 60 Days			
Total Ammonia-N[c] Remaining	145	91	122	87	100
Influent Flow, l/day	-	18.14	14.69	22.32	18.72
MLVSS'[d]	-	11350	9747	11280	10598
Specific Ammonia-Removal Rate x 10^3 $\left(\frac{\text{mg NH}_3\text{-N}}{\text{mg VSS day}}\right)$	-	3.05	1.23	4.05	2.81

[a] All values are mg/l unless otherwise stated.

[b] After 26% dilution with river water.

[c] Includes ammonia from conversion of thiocyanate.

[d] Assumes a 95% volatility for PAC.

Table 6. GC/MS ANALYSES OF INFLUENT AND REACTOR EFFLUENTS FOR PRIORITY POLLUTANTS (micrograms per litre)

		SRT = 20 Days				SRT = 60 Days			
PAC Concentration mg/l	Influent	0	1500	3000	6000	0	1500	3000	6000
Volatiles									
Acrylonitrile	16,000	-*	-	-	-	-	1,200	-	-
Methylene chloride	9	30	20	8.2	12	13	13	3.2	15
Benzene	80	38	22	98	52	30	72	36	82
Toluene	36	3.4	2.4	-	2	7.4	6	2.8	10
Ethylbenzene	11	-	-	-	-	-	-	-	1.4
Trichloroethylene	-	7.4	-	6.2	4.6	-	-	-	-
Base-neutrals									
Diethyl phthalate	17	-	220	260	130	170	0.8	260	190
Butyl benzyl phthalate	18	1.6	2.2	-	2.2	-	2.4	3.6	1.4
Di-2-ethylhexyl phthalate	520	6.2	16	11	5.8	-	110	38	12
Di-n-octyl phthalate	17	0.8	6.4	0.8	5.4	-	2	2.2	1.8
Anthracene/phenanthrene	96	0.4	1.8	3.0	1.6	2.4	0.4	2.2	2.8
Fluoranthene	76	0.4	0.2	1.8	1	0.2	0.2	0.6	0.6
Pyrene	56	1.2	0.4	1.8	1	-	0.6	0.4	0.4
Chrysene	13	1.4	0.4	5	2.8	-	0.4	0.4	0.4
Benzo[b]fluoranthene	5.6	1.2	-	9.8	6.6	-	1	1.4	-
Benzo[a]pyrene	3.2	2	-	7	5.4	-	0.8	1.8	-
Di-n-butyl phthalate	-	7.6	14	40	42	6.8	22	19	17
Benzo[k]fluoranthene	-	-	-	-	-	-	0.2	-	-
Naphthalene	-	-	-	-	4	8	-	-	-
Indeno[1,2,3-cd]pyrene	-	24	-	-	-	-	-	-	-
Benzo[ghi]perylene	-	8.8	-	-	-	-	-	-	-
Dimethyl phthalate	-	-	23	42	20	26	-	28	30
Acenaphthene	-	-	-	0.8	1	-	-	-	-
Acids									
Phenol	~110,000	200	19	-	-	1.8	6.6	-	-
2,4-Dimethylphenol	-	2.6	2.6	-	-	-	-	-	62
2-Chlorophenol	-	-	-	-	~5.4	-	-	-	-

* Dash indicates compound is below detection limits.

Table 7. RESULTS OF STATIC BIOASSAY TEST

PAC Concentration (mg/l)	Influent	SRT = 20 Days				SRT = 60 Days			
	--	0	1500	3000	6000	0	1500	3000	6000
LC 50 (Volume Percent)	1.5	27.0	29.5	63.0	-*	-*	-*	57.0	45.0

* LC 50 not encountered when less than 65 percent of the test organisms died when subjected to undiluted effluent.

Table 8. AVERAGE PERFORMANCE RESULTS OF THE PILOT-SCALE REACTORS

Parameter (mg/l)	Influent	Non-PAC Effluent	PAC Effluent
COD	2680	307	403
BOD_5	1579	22	45
TOC	616	40	48
Oil and Grease	32.4	3.2	2.7
TSS	57.5	139	175
Phenol	595	0.05	0.06
Total CN	3.4	2.3	2.1
Amenable CN	0.40	0.04	0.04
Thiocyanate	333	3	18
Ammonia-N	89	82	38

Table 9. AMMONIA-REMOVAL PERFORMANCE OF THE PILOT-SCALE REACTORS

	Influent	Non-PAC Reactor	PAC Reactor
Total Ammonia-N[a], mg/l Remaining	169	83	42
Influent Flow, l/day	-	1714	1714
MLSS, mg/l	-	10428	11640
MLVSS'[b]	-	8941	8793
Specific Ammonia Removal Rate x 10^3 $\left(\frac{\text{mg } NH_3\text{-N}}{\text{mg MLVSS-day}}\right)$		4.7	7.0

a Includes ammonia from conversion of thiocyanate.

b Assumes a 96 percent volatility for PAC.

Table 10. PRIORITY POLLUTANTS OBSERVED IN PILOT-SCALE REACTORS

SAMPLE DATE: 9/16/80
(CONCENTRATION, μg/l)

	Influent	Non-PAC Effluent	PAC Effluent
Volatiles			
Acrylonitrile	5500	210	180
Benzene	0	0	0
Methylene chloride	1	1	1
Trichloroethylene	0	0	0
Trichlorofluoromethane	0	0	0
Toluene	1	1	1
Base-neutrals			
Anthracene	40	1	1
Benzo[a]anthracene	200	70	20
Benzo[a]pyrene	30	30	1
3,4-Benzofluoranthene	30	30	1
Benzo[g,h,i]perylene	0	1	1
Benzo[k]fluorathene	20	60	20
Di-2-ethylhexyl phthalate	40	20	40
Butyl benzyl phthalate	20	1	1
Chrysene	0	0	0
Dibenzo[a,h]anthracene	0	1	1
3,3-Dichlorobenzidine	80	0	20
Diethyl phthalate	0	1	1
Di-n-butyl phthalate	0	1	1
Di-n-octyl phthalate	1	0	1
Fluoranthene	30	30	1
Indeno[1,2,3-cd]pyrene	0	1	1
Napthalene	0	1	1
N-nitrosodiphenylamine	0	20	0
Phenanthrene	0	0	0
Pyrene	30	30	1
Acid Extractables			
2-Chlorophenol	0	1	1
2,4-Dichlorophenol	1	1	1
2,4-Dimethylphenol	900	1	1
P-Chloro-m-cresol	0	1	1
Phenol	4500	1	1
2,4,6-Trichlorophenol	0	1	1

NOTE: A "0" in the table signifies that the compound was not detected in the sample. A "1" in the table signifies that the level detected was less than the screening level. Priority pollutants not detected on any of the sampling dates have been omitted from the table.

Table 11. PRIORITY POLLUTANTS OBSERVED IN PILOT-SCALE REACTORS

SAMPLE DATE: 10/1/80
(CONCENTRATION, μg/l)

	Influent	Non-PAC Effluent	PAC Effluent
Volatiles			
Acrylonitrile	5900	120	170
Benzene	0	0	0
Methylene chloride	0	1	0
Trichloroethylene	0	0	0
Trichlorofluoromethane	0	0	0
Toluene	1	0	1
Base-neutrals			
Anthracene	1	0	0
Benzo[a]anthracene	1	1	1
Benzo[a]pyrene	0	1	1
3,4-Benzofluoranthene	0	1	1
Benzo[g,h,i]perylene	0	0	0
Benzo[k]fluorathene	0	1	1
Di-2-ethylhexyl phthalate	0	1	1
Butyl benzyl phthalate	0	0	0
Chrysene	1	1	1
Dibenzo[a,h]anthracene	0	0	0
3,3-Dichlorobenzidine	0	1	1
Diethyl phthalate	0	0	0
Di-n-butyl phthalate	0	0	0
Di-n-octyl phthalate	0	0	0
Fluoranthene	1	1	1
Indeno[1,2,3-cd]pyrene	0	0	0
Napthalene	0	0	0
N-nitrosodiphenylamine	0	1	1
Phenanthrene	1	0	0
Pyrene	1	1	1
Acid Extractables			
2-Chlorophenol	0	0	0
2,4-Dichlorophenol	0	0	0
2,4-Dimethylphenol	0	0	0
P-Chloro-m-cresol	90	0	0
Phenol	3840	0	0
2,4,6-Trichlorophenol	0	0	0

NOTE: A "0" in the table signifies that the compound was not detected in the sample. A "1" in the table signifies that the level detected was less than the screening level. Priority pollutants not detected on any of the sampling dates have been omitted from the table.

Table 12. PRIORITY POLLUTANTS OBSERVED IN PILOT-SCALE REACTORS

SAMPLE DATE: 10/20/80
(CONCENTRATION, μg/l)

	Influent	Non-PAC Effluent	PAC Effluent
Volatiles			
Acrylonitrile	1690	0	0
Benzene	1	0	0
Methylene chloride	0	0	0
Trichloroethylene	0	0	0
Trichlorofluoromethane	0	0	0
Toluene	1	1	1
Base-neutrals			
Anthracene	10	0	0
Benzo[a]anthracene	20	0	1
Benzo[a]pyrene	20	1	1
3,4-Benzofluoranthene	20	1	1
Benzo[g,h,i]perylene	0	0	0
Benzo[k]fluorathene	20	1	1
Di-2-ethylhexyl phthalate	0	0	0
Butyl benzyl phthalate	0	0	0
Chrysene	30	0	1
Dibenzo[a,h]anthracene	0	0	0
3,3-Dichlorobenzidine	20	1	1
Diethyl phthalate	0	0	0
Di-n-butyl phthalate	0	0	0
Di-n-octyl phthalate	0	0	0
Fluoranthene	20	1	1
Indeno[1,2,3-cd]pyrene	0	0	0
Napthalene	0	0	0
N-nitrosodiphenylamine	0	0	0
Phenanthrene	10	0	0
Pyrene	10	1	1
Acid Extractables			
2-Chlorophenol	0	0	0
2,4-Dichlorophenol	1	0	0
2,4-Dimethylphenol	2750	0	1
P-Chloro-m-cresol	0	0	0
Phenol	11810	1	0
2,4,6-Trichlorophenol	0	0	0

NOTE: A "0" in the table signifies that the compound was not detected in the sample. A "1" in the table signifies that the level detected was less than the screening level. Priority pollutants not detected on any of the sampling dates have been omitted from the table.

Table 13. PRIORITY POLLUTANTS OBSERVED IN PILOT-SCALE REACTORS

SAMPLE DATE: 10/30/80
(CONCENTRATION, μg/l)

	Influent	Non-PAC Effluent	PAC Effluent
Volatiles			
Acrylonitrile	1180	250	0
Benzene	1	1	1
Methylene chloride	1	1	1
Trichloroethylene	10	1	1
Trichlorofluoromethane	1	1	1
Toluene	1	1	1
Base-neutrals			
Anthracene	0	0	0
Benzo[a]anthracene	1	1	10
Benzo[a]pyrene	1	0	20
3,4-Benzofluoranthene	1	1	10
Benzo[g,h,i]perylene	0	0	1
Benzo[k]fluorathene	0	0	0
Di-2-ethylhexyl phthalate	0	0	0
Butyl benzyl phthalate	0	0	1
Chrysene	1	1	20
Dibenzo[a,h]anthracene	0	0	0
3,3-Dichlorobenzidine	0	0	0
Diethyl phthalate	0	0	0
Di-n-butyl phthalate	0	1	1
Di-n-octyl phthalate	0	0	0
Fluoranthene	20	70	820
Indeno[1,2,3-cd]pyrene	1	0	20
Napthalene	0	0	0
N-nitrosodiphenylamine	0	0	0
Phenanthrene	0	0	0
Pyrene	1	1	10
Acid Extractables			
2-Chlorophenol	0	0	0
2,4-Dichlorophenol	1	0	0
2,4-Dimethylphenol	1220	0	1
P-Chloro-m-cresol	0	0	0
Phenol	6680	1	1
2,4,6-Trichlorophenol	0	0	0

NOTE: A "0" in the table signifies that the compound was not detected in the sample. A "1" in the table signifies that the level detected was less than the screening level. Priority pollutants not detected on any of the sampling dates have been omitted from the table.

Table 14. FLOW-THROUGH BIOASSAY RESULTS USING PILOT-REACTOR EFFLUENTS

REACTOR DESIGNATION	Percent Affected Organisms in Undiluted Effluent	LC 50* (Volume Percent)
BIOASSAY I (9/25/80)		
Non-PAC	65	Not encountered
PAC	20	Not encountered
BIOASSAY II (10/25/80)		
Non-PAC	15	Not encountered
PAC	100	49

* LC 50 not encountered when less than 65 percent of the test organisms died when subjected to undiluted effluent.

BIOLOGICAL TREATMENT OF BY-PRODUCT COKE PLANT WASTEWATER FOR THE CONTROL OF BAT PARAMETERS

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ABSTRACT

This paper presents the findings of an evaluation of the activated sludge process for the treatment of coke plant wastewaters (CPW) to meet compliance with BAT limitations for conventional/non-conventional parameters. The evaluation entailed the operation of batch and continuous flow laboratory scale reactors, and a 50 gpd pilot plant.

The study produced understandings of (a) the sequence in which the different components in CPW are removed, (b) the order of the degradation reaction associated with each component, (c) the potential inhibitory effects of different CPW components on the different degradation reactions, and (d) kinetic expressions associated with treatment rates and sludge production which could be used to design the biological treatment system.

INTRODUCTION

The treatment of wastewaters from coke and coal carbonization plants is not new. Some of the earliest treatment studies of waste liquors from these plants were conducted during the early 1900s. In a 1907 report, Frankland and Silvester(1) concluded, "considerable but not insuperable difficulties (exists) in the purification of (gas liquor wastes) by bacterial means; on the other hand, the oxidation of these wastes by chemical means can only be effected at a prohibitive cost." Today 74 years later, in spite of all of the work conducted, many of these difficulties persist and they are the causes of concern regarding compliance with the impending "best available technology" (BAT) discharge limitations. These limitations will require controls on several specific pollutants (conventional and priority); this report addresses only the conventional pollutants -- ammonia, cyanide, phenol, oil & grease, and suspended solids.

Despite the long history of investigations into the biological treatment of coke plant wastewaters (CPW), treatment facilities have not been designed or operated to produce effluent quality which approaches that required by the proposed BAT limitations. Without this prior experience and/or a comprehensive knowledge of the biological reactions involved in this mode of treatment, the design and operation of treatment systems to consistently produce compliance with BAT requirements will be difficult.

In order to gain a better understanding of the biological treatment of coke plant wastewaters this study was initiated. This understanding would provide the basis for the design and operation of treatment facilities which may be capable of producing compliance with impending BAT limitations. To achieve this objective the following information was sought:

- The order of the different reactions,
- The sequence in which the reactions occur and which reaction(s) is the limiting step,
- The effects of different wastewater components on different reactions, and
- The relationship between operating parameters such as mixed liquor solids, hydraulic and sludge residence time, and treatment performance.

This study examined the biological treatment of CPW in a single stage activated sludge treatment process for the control of ammonia, free cyanide, phenol and thiocyanate.

The study entailed a review of the published literature, laboratory scale experiments with both batch and continuous flow reactors, and a 50 GPD pilot plant which was located on-site at a coke plant. This report presents the findings of this study.

Subsequent sections of this report will present:

- A brief review of the public literature,
- Results of the experimental program, and
- A discussion of the application of the experimental data to design a BAT biological system for CPW.

LITERATURE REVIEW

Coke plant wastewater (CPW) contain many components which are of concern from a pollutional standpoint; thus, their discharge will be regulated. Further, many of these components may exert inhibitory effects on the different biological reactions in the course of the treatment process. Thus, in attempting to achieve effective treatment many process modes have been examined. For example:

- Kostenbader and Flecksteiner(2) found it was necessary to dilute waste ammonia liquor (WAL) to ammonia concentration less than 2000 mg/l to achieve phenol removal,
- Biczysko and Suschka(3) achieved effective phenol removal from undiluted wastewater which contained ammonia concentrations of 150-2280 mg/l,

- Barker and Thompson(4) evaluated the treatment of WAL in a multi-staged reactor system with limited success,
- Catchpole and Cooper(5) examined "growth factors" as means of enhancing/accelerating the biological treatment process; their results were inconclusive, and
- Luthy et al(6) demonstrated the nitrification of coke plant waste in a single stage reactor; reactor conditions were 40 days SRT and 9 days HRT.

The first two studies were primarily concerned with achieving phenol removal; the latter three studies were directed at achieving advanced treatment--control of ammonia, cyanide, phenol, and thiocyanate. For the composition of the raw wastewater (ammonia about 100 mg/l) used in the investigation of Luthy et al(6), the 9 day HRT required for achieving nitrification is economically impractical, and at best this study illustrates advanced treatment in a single stage reactor is achievable. The limited success in the reported studies is ample evidence that the status of the understanding of advanced biological treatment of coke plant wastewaters is still very primative. Subsequent discussions will attempt to further the present status.

EXPERIMENTAL BIOTREATMENT OF CPW

MATERIAL AND METHODS

The experimentation entailed the following:

- Treatment of both synthetic and actual CPW,
- Operation of laboratory scale batch and continuous flow reactors, and
- Operation of a 50 GPD pilot treatment system at a coke plant.

All reactors were operated at temperatures about 20-25°C, pH about 7.0-7.5 and D.O. concentrations ~ 2.0 mg/l.

The synthetic wastewater was formulated with essential components being ammonia, free cyanide, phenol and thiocyanate. The concentration of these components were varied as required. The CPW wastewater used was that produced after ammonia stripping; the composition was ammended as required. Phosphorus was also added to the CPW as a nutrient. Table 1 presents the average composition of the wastewaters used in this study.

The sludge used in this study was obtained from an activated sludge system treating coke plant wastewater. This sludge was allowed to acclimate to CPW until an effective nitrifying population was established. This acclimation took about 4 to 6 weeks because the original sludge was not actively nitrifying. The continuous flow reactor experiments were conducted for a minimum period of about 10 to 12 weeks under a given set of conditions before changes to another set were made. While these test periods were significantly less than three times the sludge retention time (SRT), it was significantly greater than three times the hydraulic residence time (HRT). No attempt was made to operate for 3 times SRT because it was felt that the biological populations were sufficiently stable after the initial development of the microbial population and the acclimation to the test conditions under consideration.

TABLE 1. AVERAGE COMPOSITION OF THE WASTEWATERS USED IN THE CONTINUOUS FLOW EXPERIMENTS

	Synthetic	Coke Plant		
		ASW 1	ASW 2	Pilot Plant
		(all concentrations mg/l)		
Ammonium-N	205	93	249	100
Free Cyanide, CN_F	182	82	72	1
Phenol, OH	1121	1113	1163	500
Thiocyanate, SCN^-	522	524	607	220
$^*\Sigma N_{in}$	429	264	434	153
**pH	9.5 & 10.5	9.7	9.7	9.0

$^*\Sigma N_{in} = (NH_4^+ - N) + 0.54\ CN_F + 0.24\ SCN$

**The pH of synthetic waste was changed from 9.5 to 10.5 for two sets of experiments.

BATCH REACTOR EXPERIMENTS

A batch reactor experiment entailed monitoring of a component(s) with the passage of time. The experiments were prepared by adding an aliquot of wastewater to an aliquot of acclimated sludge. From these experiments it was possible to establish the following:

- Reaction order for each component,
- Reaction sequence, and
- Tolerence limits for different components on individual reactions.

These experiments were facilitated by using synthetic wastewaters. However, spot tests with CPW were in complete agreement with the observations made with the synthetic wastewaters.

Types of Reaction and Reaction Sequence

Figures 1 and 2 show typical depletion profiles for (a) ammonia, (b) free cyanide, (c) phenol, and (d) thiocyanate. These profiles show the ammonia, phenol and thiocyanate reactions to be zero order and the cyanide reaction to be first order. The profiles in Figure 2 illustrate the

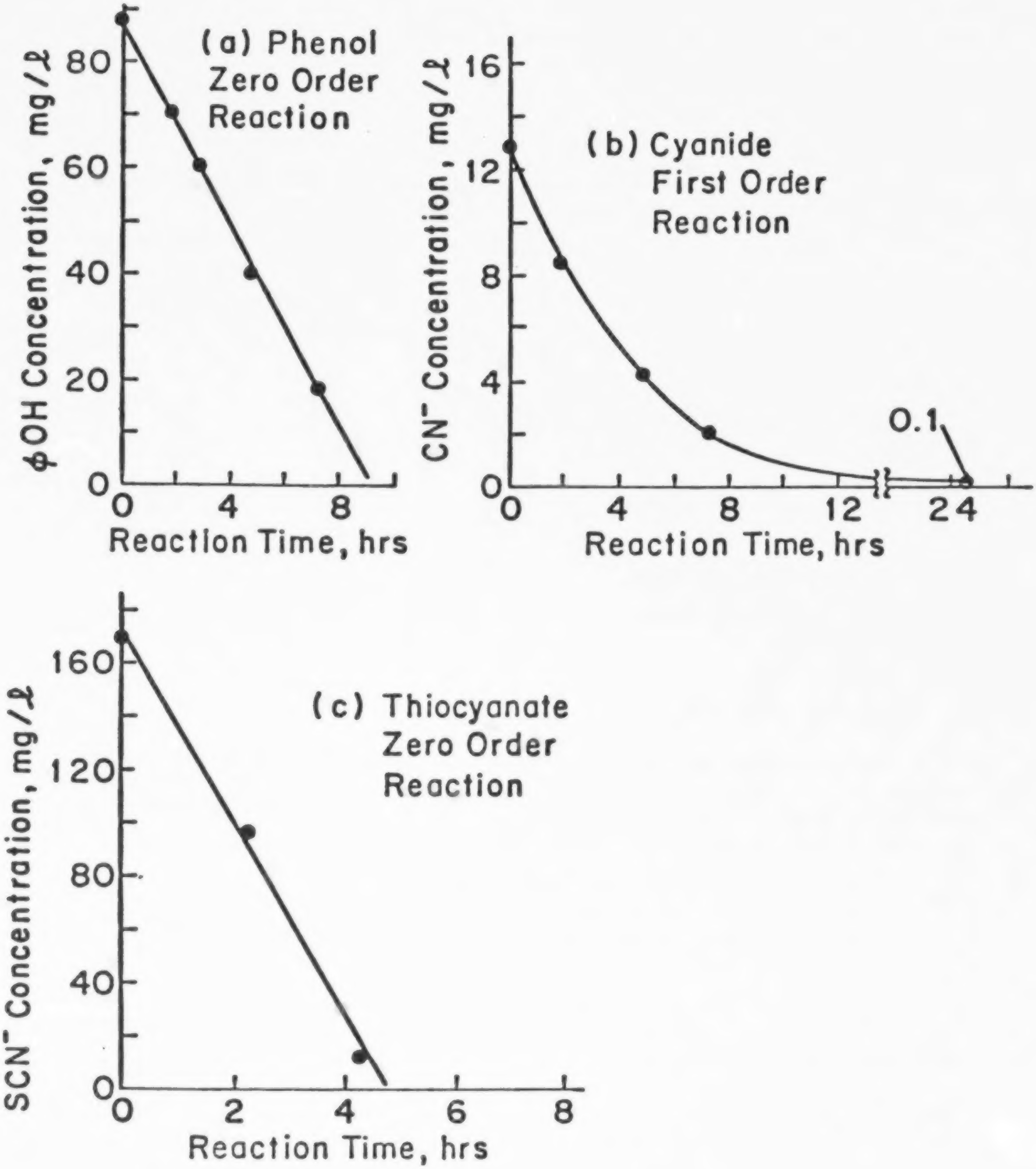

Figure 1. Depletion profiles for phenol, cyanide and thiocyanate by acclimated sludge

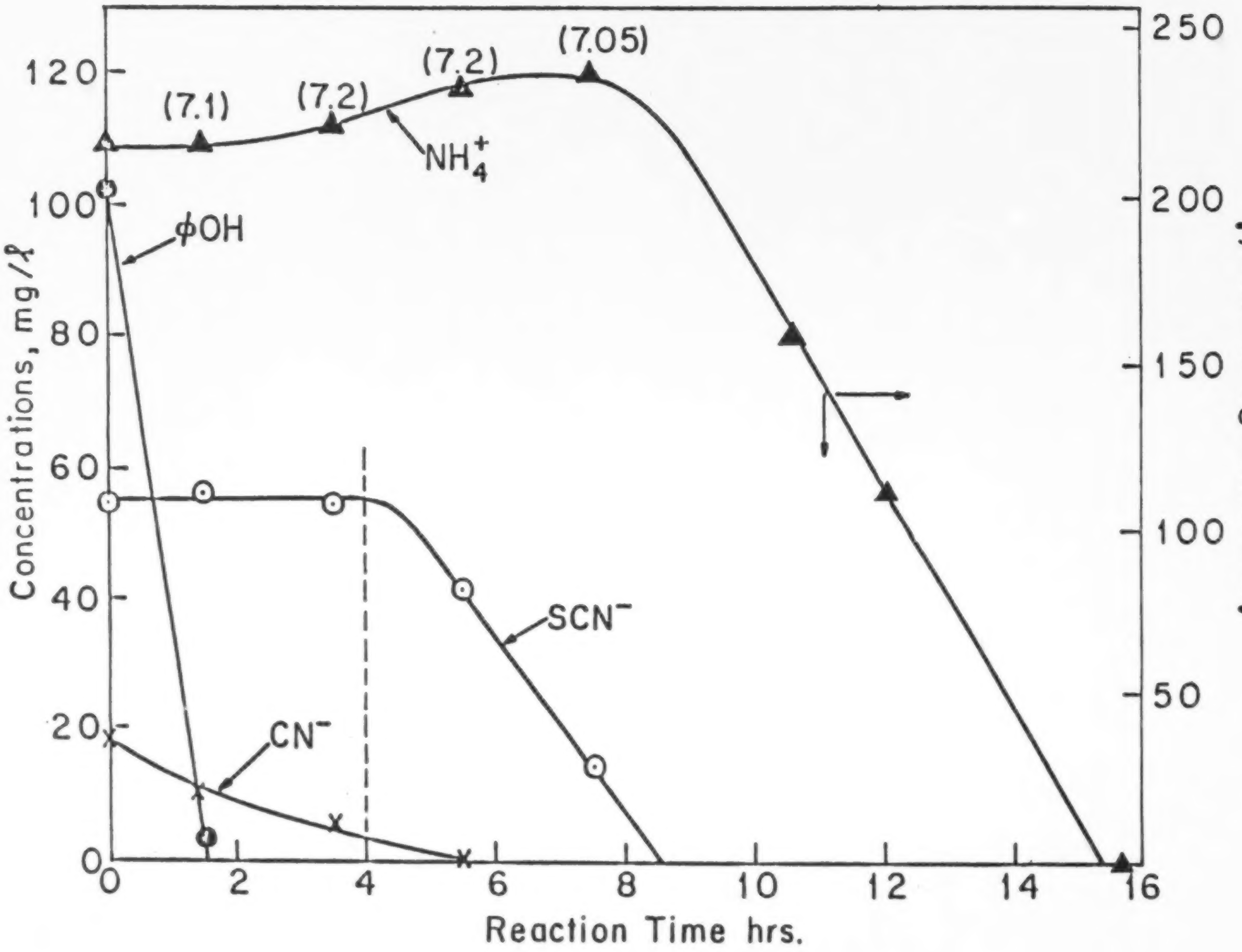

Figure 2. Reaction sequence for ammonia, cyanide, phenol and thiocyanate in a batch reactor

sequence of the reactions as they occur in a batch biological reactor treating coke plant wastewater. The sequence shows that ammonium oxidation is the last reaction to occur. Consequently, for advanced biological treatment of coke plant wastewater the ammonium oxidation reaction would be the process limiting reaction and process design criteria based on the ammonium oxidation reaction would accommodate the degradation of the other components -- cyanide, phenol and thiocyanate.

The ammonium profile in Figure 2 shows a gradual increase during the early stages of the experiment. This increase corresponds with the ammonia produced during the degradation of cyanide and thiocyanate.

Reaction Interactions

The profiles in Figure 2 also show that the microorganisms responded to both phenol and cyanide immediately. This occurrence suggests that the concentrations of phenol examined were not inhibitory to cyanide degradation or vice versa. Experiments with initial phenol concentration up to 110 mg/l and cyanide concentrations of 20 mg/l shows similar uninhibited responses. On the other hand, the lag segment of the thiocyanate profile (see Figure 2), indicate the inhibitory effect of cyanide at concentrations greater than 3.0 mg/l; the nitrification reaction was inhibited by cyanide concentrations greater than 0.5 mg/l. The data in Figure 2 does not show any inhibitory effects for phenol; this observation is due to the rapid rate at which the phenol was degraded. However, it must be recognized that phenol can inhibit the nitrification reaction(7).

In other experiments where thiocyanate inhibition of the nitrification reaction was examined, it was observed that the inhibition was not as dramatic as that from cyanide. In fact, the nitrifying organisms were capable of adpating to thiocyanate concentrations as high as 200 mg/l; Downing et al(7) reported inhibition to nitrification in activated sludge at <300 mg/l. Consequently, in the operation of a biological treatment system to achieve effective advanced treatment it will be necessary to accommodate for the potential inhibitory effects of cyanide, phenol and thiocyanate. This accommodation can be achieved by developing treatment process design criteria which considers the nitrification reaction(s) as the process controlling step.

CONTINUOUS FLOW REACTION EXPERIMENTS

The continuous flow experiments were conducted in completely mixed reactors with integral clarifiers, Figure 3. These experiments were designed to establish performance trends associated with variations in feed flow rate, feed composition and mixed liquor solids concentration. A reactor's performance was measured by material balances on oxidizable nitrogen and biological solids.

Oxidizable Nitrogen Oxidation

In the biological treatment of free cyanide and thiocyante, ammonia is produced; this ammonia production is almost stoichiometric in quantity.

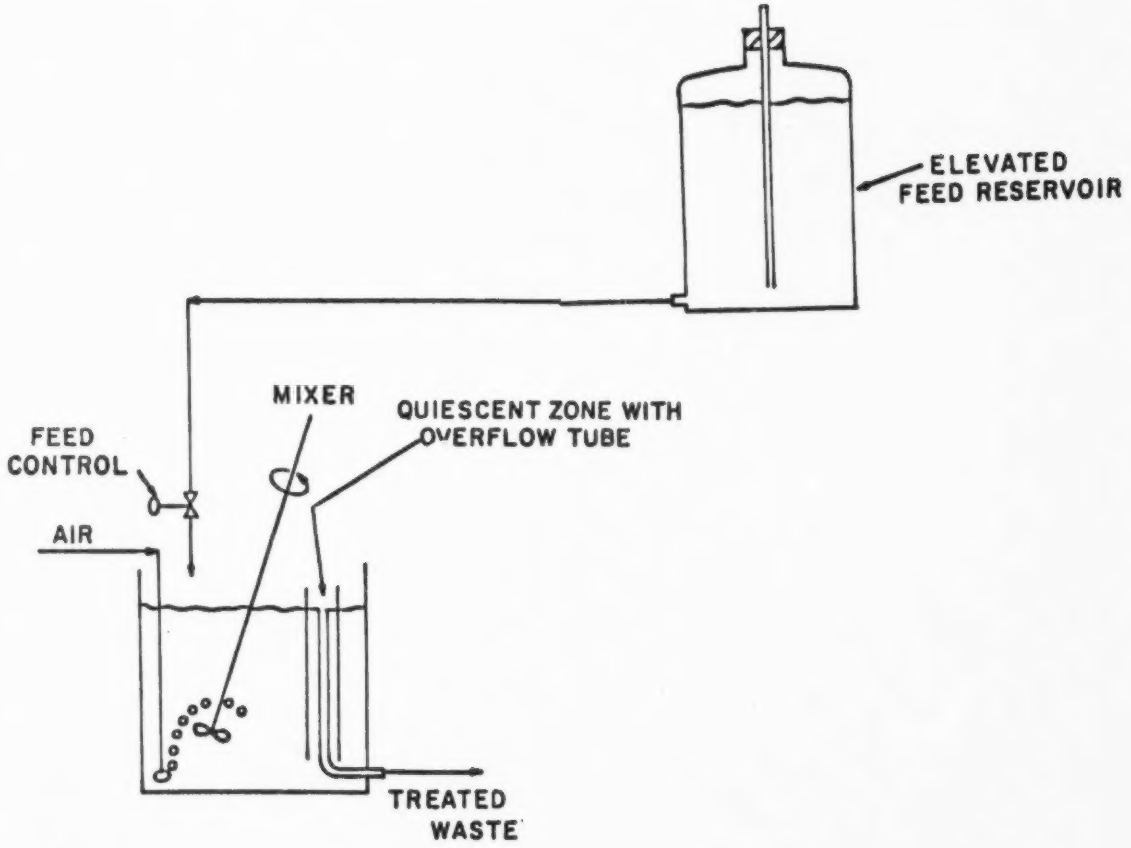
ELEVATED
FEED RESERVOIR
MIXER
QUIESCENT ZONE WITH
OVERFLOW TUBE
FEED
CONTROL
AIR
TREATED
WASTE

Figure 3. Schematic flow diagram of laboratory scale reactors

Thus, in advanced biological treatment of CPW for the control of ammonia, that produced from cyanide and thiocyanate must also be considered. The total ammonia or oxidizable nitrogen in the wastewater can be estimated by

$$\Sigma N = (NH_4^+ - N) + 0.24\ SCN + 0.54\ CN_F \qquad \ldots.(1)$$

The reaction sequence shown in Figure 2 indicates that the nitrification reaction is the process controlling step and the reaction is zero order with respect to oxidizable nitrogen. Thus a material balance for oxidizable nitrogen around a continuous flow reactor at steady state can be mathematically expressed as

$$\Sigma N_{out} = \Sigma N_{in} - k_A \tau \qquad \ldots.(2)$$

where

N_{in} = feed oxidizable nitrogen concentration,
N_{out} = reactor oxidizable nitrogen concentration,
k_A = rate of oxidation at a specified mixed liquor solids concentration,
τ = reactor hydraulic residence time.

In all of the experiments conducted, the concentration of phenol, free cyanide and thiocyanate in the reactor at steady state were less than 0.1, 0.1 and 1.0 mg/l respectively. Thus, the oxidizable nitrogen in the reactor was essentially the reactor ammonium concentration. Thus Equation 2 can be rewritten as

$$k_A = \frac{\Sigma N_{in} - (NH_4^+ - N)}{\tau} \qquad \ldots.(3)$$

where $(NH_4^+ - N)$ = reactor ammonium-nitrogen concentration.

Several reactor conditions (hydraulic residence time, mixed liquor solids, raw waste composition and sludge residence times) were examined and the results of these are presented on Figure 4 where oxidation rate, k_A is correlated with mixed liquor solids.The regression analysis produced the following relationship:

$$k_A = 0.015\ TVS - 0.0045 \qquad \ldots.(4)$$

The correlation coefficient, r, was 0.96. However, the k_A value of -0.0045 at zero TVS may be an artifact of the regression analysis, thus Equation 4 will be truncated to read:

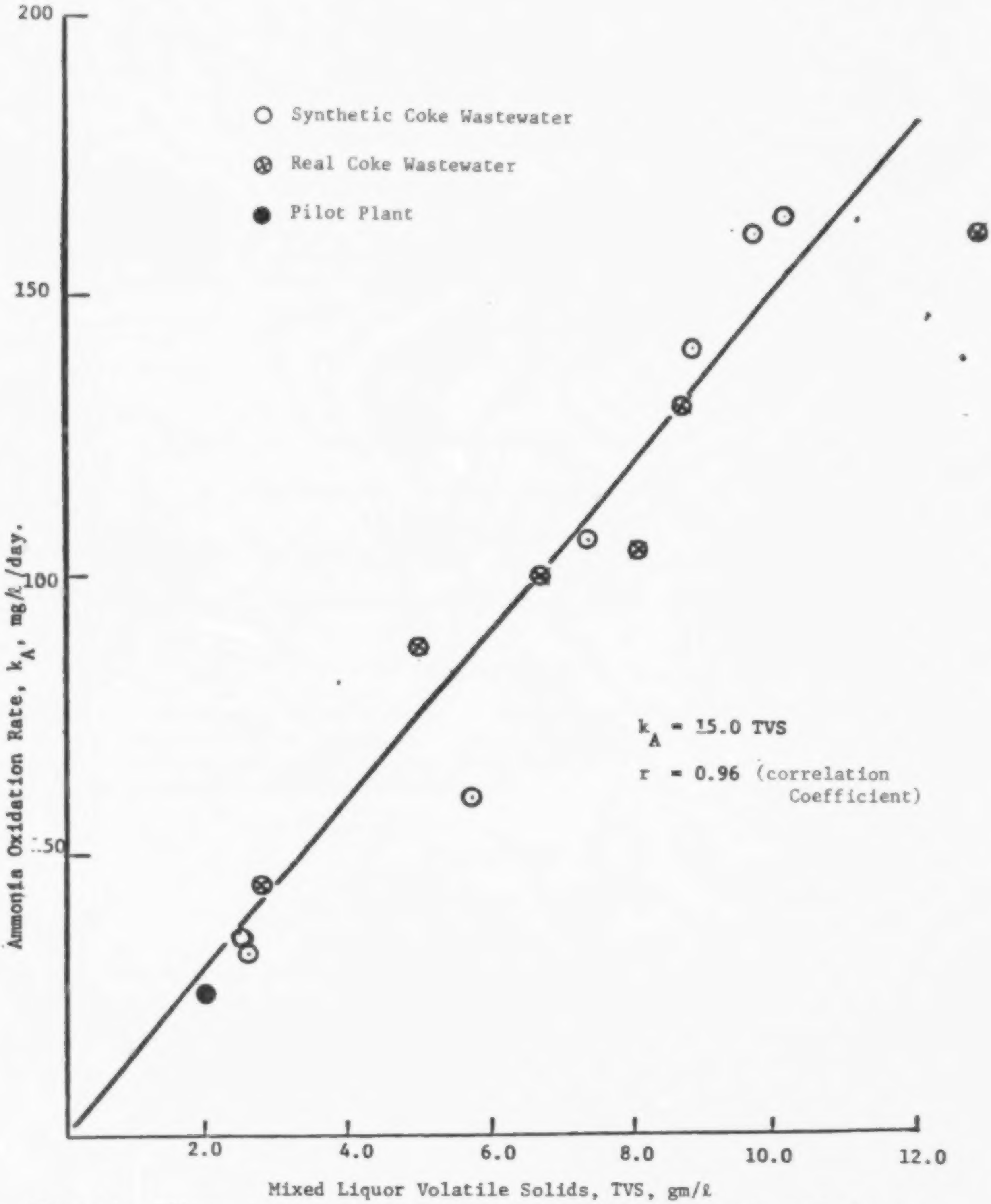

Figure 4. Effect of mixed liquor solids concentration on ammonia oxidation rate

$$k_A = 0.015 \text{ TVS} \qquad \text{....(5)}$$

where

TVS = mixed liquor volatile solids concentration, mg/l

Biological Sludge Growth

In biological wastewater treatment processes, the microorganisms use a fraction of the energy produced by the metabolic reactions for cell growth and reproduction, and the remaining fraction for maintenance of other cellular functions. Biological sludge growth in the activated sludge process has been expressed as

$$\frac{1}{\theta} = Y_e U - b \qquad \text{....(6)}$$

where b = microbial maintenance energy coefficient, day^{-1}

U = specific substrate utilization rate, day^{-1}

Y_e = observed sludge yield

θ = sludge residence time, days

Figure 5 presents the sludge growth relationships observed in this study; these are:

$$\theta^{-1} = 0.019\ Y_e - 0.0012 \qquad \text{....(7)}$$

The value 0.019 day^{-1} for U compares well with 0.015 day^{-1} produced by the correlation of k_A vs TVS (see Figure 4). From equation 7, values for Y_{max} and b are estimated at 0.65 and 0.0012 respectively. Consequently for any given set of operating conditions, the sludge production rate can be estimated from

$$S_p = F(\Sigma N_{in} - \Sigma N_{out})Y_e \qquad \text{....(8)}$$

where S_p = sludge production rate.

DESIGN OF A BAT BIOTREATMENT SYSTEM FOR COKE PLANT WASTEWATERS

Equations 3, 5, 7, and 8 are the essential relationships for designing a coke plant wastewater biological treatment system. These equations can be used to size the aeration basin and to determine the amount of sludge produced. Other data necessary to complete the design would be (a) oxygen up-take rates, and (b) sludge settling characteristics; these data are required for sizing/specifying the aeration device and sludge clarifier.

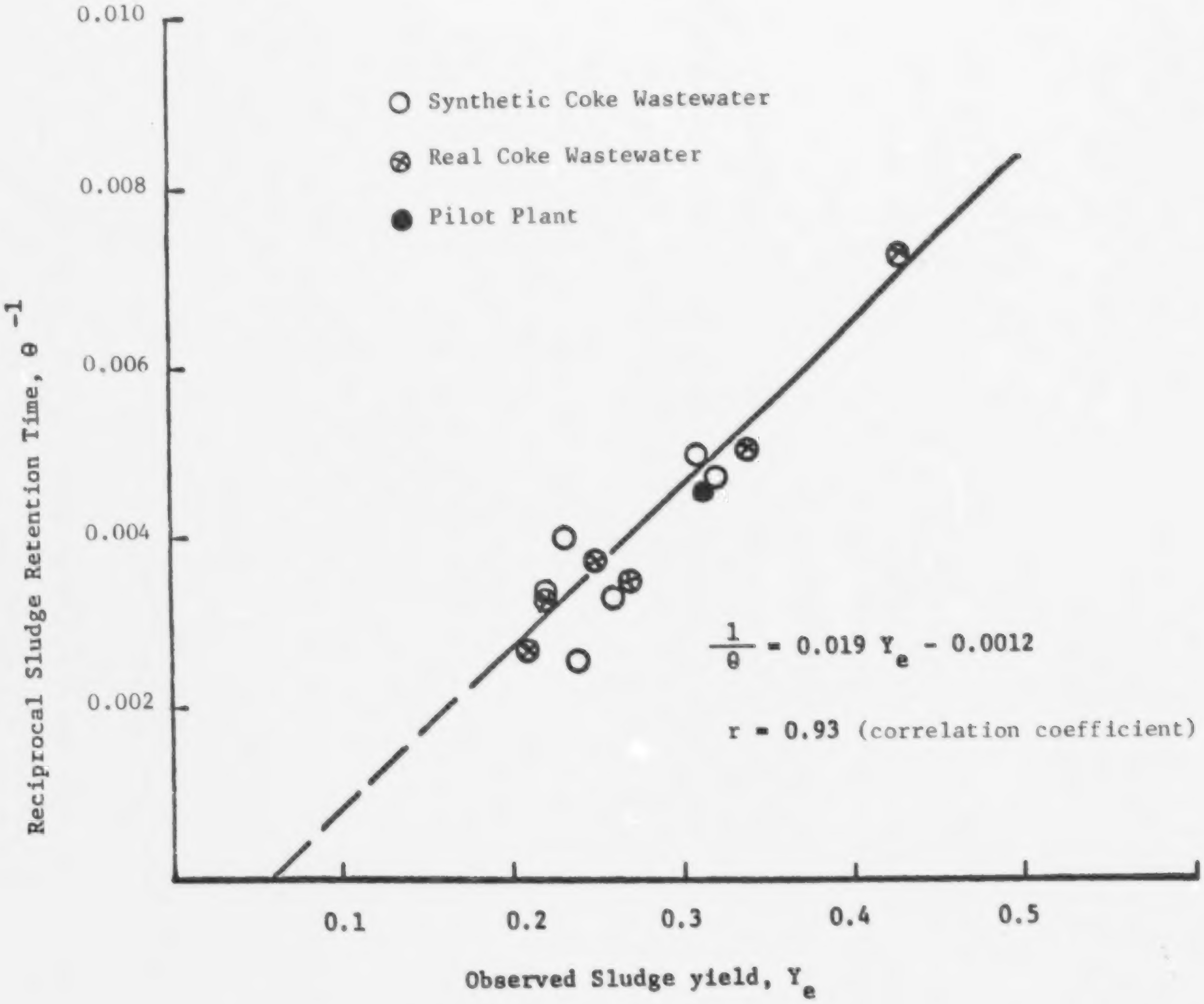

Figure 5. Sludge yield/sludge retention time relationship

From Equation 5, oxidation rates can be determined for specified mixed liquor solids; these oxidation rates can then be applied to Equation 3 to determine aeration basin hydraulic residence times (HRT) for the desired treatment. In turn, the HRTs can be used to determine the size of the aeration basin, given the quantity of wastewater to be treated.

From Equation 7 a limiting sludge residence time (SRT) can be determined; i.e., that at which Y_e is equal to Y_{max} (0.65). Operations at SRT conditions less then this limiting SRT will result in the loss of the mixed liquor solids by washout with a concommitant loss in treatment performance. Equation 7 also predicts that at long SRTs, Y_e will be small which will result in small sludge generation.

CONCLUSIONS

A single stage activated sludge process was examined for the treatment of CPW for the control of BAT conventional and non-conventional parameters -- ammonia, free cyanide, phenol and thiocyanate. The study was conducted by observing the performances of batch and continuous flow laboratory scale reactors and a 50 gpd pilot plant.

The study produced knowledge of:

- The sequence in which the different components in CPW are removed,
- The potential inhibitory effects of different CPW components on the different degradation reaction, and
- Kinetic expressions which define treatment performance and sludge generation in the process.

In addition, this laboratory scale study demonstrated that if the treatment system is designed and operated for ammonia oxidation, treatment of free cyanide, phenol, and thiocyanate are achieved; treated effluent concentrations for these parameters were observed in this study to be less than 0.1, 0.1 and 1.0 mg/l respectively. However, this treatment/design approach should be tested in a full scale plant operation.

ACKNOWLEDGEMENT

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TWO-STAGE BIOLOGICAL FLUIDIZED BED TREATMENT OF COKE PLANT WASTEWATER FOR NITROGEN CONTROL

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INTRODUCTION

Wastewaters from steel mill coking operations contain high concentrations of phenolics, thiocyanates, ammonia, cyanide, sulphides and a variety of complex hydrocarbons. Of the steel mills in North America which employ biological systems for oxidation of phenolics, thiocyanates, cyanide and sulphides, the majority utilize the activated sludge process (1). None of these systems consistently effect a significant degree of nitrogen control (2). Researchers (3,4,5) have shown that complete nitrification of coke plant effluents can be attained under various conditions in either two-stage or single-stage biological systems.

Bridle et al (6,7) demonstrated that complete nitrogen control was feasible in a single sludge pre-denitrification-nitrification configuration provided that wastewater dilution or powdered activated carbon addition (PAC) was practised in conjunction with strict SRT control. Medwith and Lefelhocz (8) were able to nitrify coke plant wastewaters in a hybrid suspended growth-fixed film biological system by the addition of an inert particulate, such as coke breeze or coal dust to a conventional activated sludge system. It was found that the inert material facilitated operation at long SRT's (50 to 200 days) and allowed complete nitrification to occur at nominal hydraulic retention times in the range of 12 to 24 hours for coke plant wastewaters diluted in the range of 1 to 5 parts wastewater per one river water.

The biological fluidized bed process has been demonstrated to be feasible for carbon removal from municipal (9,10,11) and concentrated industrial wastes (12), for nitrification (9,13) and for denitrification (14,15) of a variety of low and high strength wastewaters. The fluidized bed system, in specific instances, can provide significant advantages relative to suspended growth systems due to the high biomass concentrations which can be maintained in the biological reactors. In order to assess the technical and economic feasibility of treating coke plant wastewaters in a two-stage fluidized bed system operated in the pre-denitrification-nitrification mode, a pilot-scale investigation of the process is being conducted at the Environmental Protection Service's Wastewater Technology Centre (WTC) in Burlington, Canada.

The primary objective of the initial stages of the investigation has been to establish the minimum hydraulic retention times required in each reactor to maintain adequate nitrogen control during treatment of undiluted coke plant wastewaters. The preliminary results of these on-going investigations are the topic of this paper.

DESCRIPTION OF PILOT-SCALE FLUIDIZED BED SYSTEM

The fluidized bed process is a modification of more conventional fixed film processes, such as the trickling filter, in which wastewater is passed upward through a bed of granular support media, typically sand, at a sufficient velocity to expand or fluidize the media. The granular media provides a large surface area for the establishment of a biological film. The pilot-scale system under examination at WTC consists of two fluidized bed reactors in series, coupled to provide carbon oxidation, nitrification and denitrification in the pre-denitrification operating mode. In this flow configuration, the supplemental carbon requirements for denitrification are minimized as the organic carbon in the raw wastewater provides the energy source and serves as the electron donor for the denitrification reaction. Full-scale industrial experience (16) and cost comparisons based on municipal systems (17) have indicated the potential of the pre-denitrification process for nitrogen control.

The process flowsheet of the coupled, two-stage fluidized bed pilot plant is shown in Figure 1. The pilot plant consists of an anoxic denitrification fluidized bed reactor, 150 mm in diameter, and an oxygenic nitrification fluidized bed reactor, 290 mm in diameter. The initial empty bed reactor volumes were 58.5 litres and 210 litres for the anoxic and oxygenic beds respectively; however, the bed heights and reactor volumes are adjustable by relocation of the position of the sand-biomass separation systems. Pure oxygen is supplied to the nitrification reactor through a proprietary oxygen transfer device provided by Dorr-Oliver Inc. High internal recycle rates are necessary for both reactor to maintain the required fluidization fluxes, to ensure an adequate supply of oxygen to the nitrification process and to return nitrate and nitrite to the denitrification reactor. The support media in both reactors is quartzite sand with an effective size of 0.48 mm.

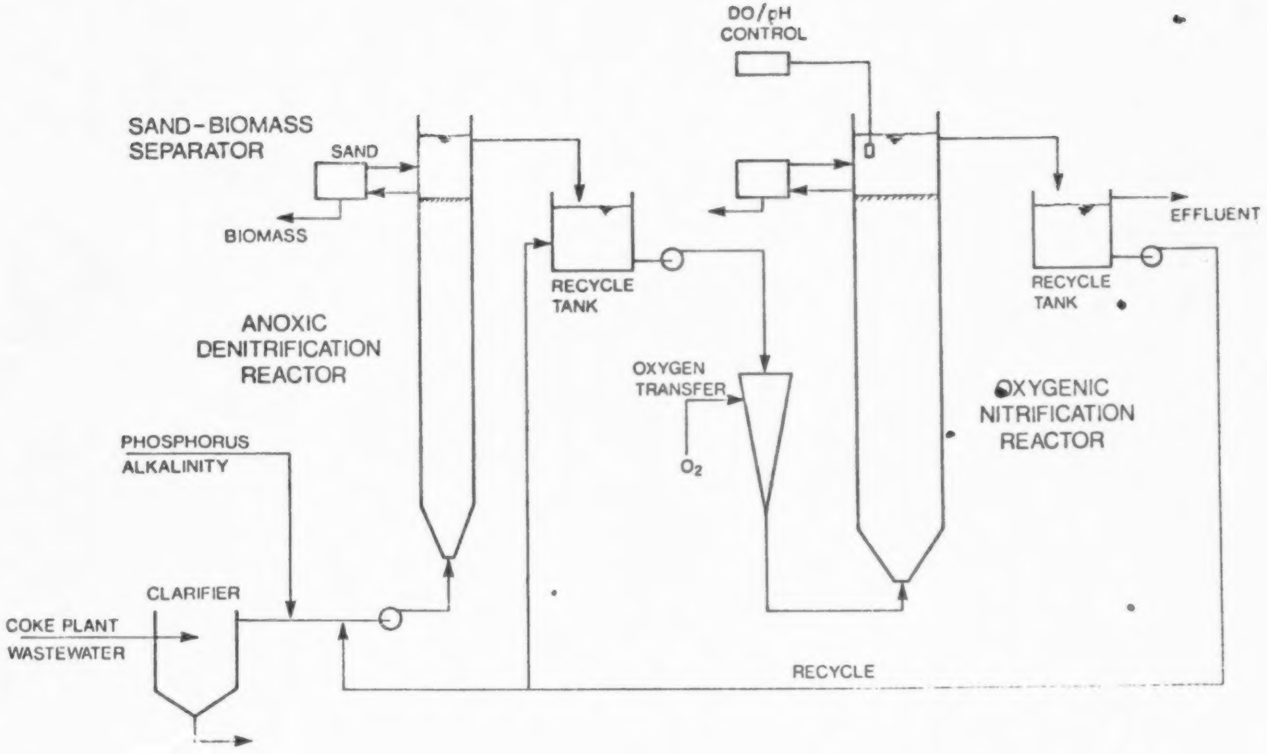
DO/pH CONTROL
SAND-BIOMASS SEPARATOR
SAND
BIOMASS
RECYCLE TANK
EFFLUENT
RECYCLE TANK
ANOXIC DENITRIFICATION REACTOR
OXYGEN TRANSFER
O_2
OXYGENIC NITRIFICATION REACTOR
PHOSPHORUS
ALKALINITY
CLARIFIER
COKE PLANT
WASTEWATER
RECYCLE

Figure 1. Two-Stage Biological Fluidized Bed Process Flowsheet.

The raw feed to the pilot-scale treatment system consists of limed ammonia still effluent and light oil interceptor sump wastewater obtained, on a batch basis, from Dofasco Inc. in Hamilton, Ontario. This is the same wastewater source used by Bridle et al (6,7) in the evaluation of the single sludge suspended growth biological treatment process. The feed undergoes primary clarification prior to entering the denitrification reactor. Phosphorus is added in the form of phosphoric acid on a continuous basis to maintain 1 to 2 $mg \cdot L^{-1}$ of soluble phosphorus in the treated effluent. In addition, there are automatic dissolved oxygen and pH control systems on the nitrification reactor. Control of pH is by means of sodium biocarbonate addition, which also provides supplemental alkalinity for the nitrification reactions.

EXPERIMENTAL AND ANALYTICAL PROCEDURES

Subsequent to an extended acclimation period to establish viable populations of micro-organisms in each fluidized bed reactor, the treatment system was operated at a number of pseudo-steady state loading conditions to define process performance. Daily samples of treated process effluent were collected at each pseudo-steady state condition and analyzed for filterable organic carbon (FOC), ammonia-nitrogen (NH_3-N), nitrate (NO_3-N) and nitrite (NO_2-N) nitrogen, total and filterable Kjeldahl nitrogen (TKN), phosphorus and alkalinity. In addition, treated effluents were analyzed three times per week for phenol, total and filterable chemical oxygen demand (COD), total cyanide (TCN), thiocyanate (CNS) and sulphide. Total and volatile suspended solids analyses were conducted five times per week.

Effluent from the anoxic denitrification reactor was monitored daily for FOC, NO_3-N, NO_2-N and TKN. The quality of the raw feed to the system was monitored on a weekly basis for FOC, TKN, NH_3-N, TCN, CNS, COD, pH and alkalinity. The concentration of biomass (bed volatile solids, BVS) in each reactor was measured once per week, based on compositing at least three individual samples from various positions in the reactors. All analyses were conducted according to standard procedures (18).

Pseudo-steady state conditions were assumed to have been attained when, after a step change in the process loading, the final effluent NH_3-N concentration had stabilized at a constant level. This typically required from twenty to forty days, depending on the magnitude of the step change. Pseudo-steady state performance data were collected for one to three weeks at each loading condition. These data do not represent true steady state in terms of the biomass as a constant biomass concentration and equilibrium SRT were not attained in the reactors.

All pseudo-steady state performance data presented in this paper were collected from the same batch of coke plant wastewater obtained from Dofasco in November 1980. The quality of the feed varied slightly during this operating period due to freezing of the wastewater and some losses of volatile compounds, in particular, ammonia. The average quality of the wastewater, based on the weekly analyses, is summarized in Table 1 and was similar to that reported by Bridle et al (7). The removal efficiencies reported for the pseudo-steady state experiments are based on the raw feed quality measured during the specific period of operation under consideration.

TABLE 1. COKE PLANT WASTEWATER CHARACTERISTICS

Parameter	Average Conc. ($mg \cdot L^{-1}$)	Median Conc. per Bridle *et al* (7) ($mg \cdot L^{-1}$)
FOC	824.	680.
Phenol	560.	300.
TKN_{UF}	214.	--
TKN_{F}	207.	180.
NH_3-N	84.6	88.
TCN	9.0	8.
CNS	381.	240.
COD_{UF}	3395.	--
COD_{F}	3194	--

RESULTS

START-UP AND ACCLIMATION

The fluidized bed reactors were started up in June 1980 using sand obtained from a Dorr-Oliver pilot scale fluidized bed which had been operated for combined carbon removal and nitrification of municipal wastewaters. The reactors were filled to the 2 m height with seeded sand and hydraulically expanded by fifty percent for the acclimation period. Feed at start-up was Dofasco coke plant wastewater diluted in the ratio of 19:1 with secondary effluent from a pilot scale extended aeration plant treating municipal wastewater.

As shown in Figure 2, the system acclimated rapidly to the coke plant wastewater. Within twenty days, the biomass concentration in both reactors had approximately doubled. Significant production of oxidized nitrogen (nitrite and nitrate) was evident in the oxygenic reactor within five days, and the nitrification rate gradually increased during the initial twenty days of operation. During this period, the ratio of dilution water to coke plant wastewater was gradually decreased from 19:1 to 5:1.

Between the twentieth and fortieth day of the acclimation period, the degree of dilution was further reduced until, by Day 40, the system was operating on full strength coke plant wastewater. Some inhibition of nitrification was evident as the amount of dilution was reduced; however, the process rapidly recovered and appeared to be completely acclimated to the coke plant wastewater after forty days of operation.

PSEUDO-STEADY STATE PERFORMANCE

To date, process performance has been assessed under four different pseudo-steady state operating conditions which are summarized in Table 2.

The initial steady state run (Run 1) was conducted at loading conditions similar to those specified by Bridle et al (7) as necessary to maintain consistent nitrification in suspended growth systems. The total system hydraulic retention time (HRT) for Run 1 was approximately 45 hours (1.9 days), where the system HRT is defined as the HRT in the anoxic denitrification reactor plus the HRT in the oxygenic nitrification reactor. The reactor HRT is based on the flow rate of coke plant wastewater and the empty bed reactor volume. In each subsequent run, the hydraulic and contaminant loadings were increased in an effort to define the minimum reactor HRT requirements.

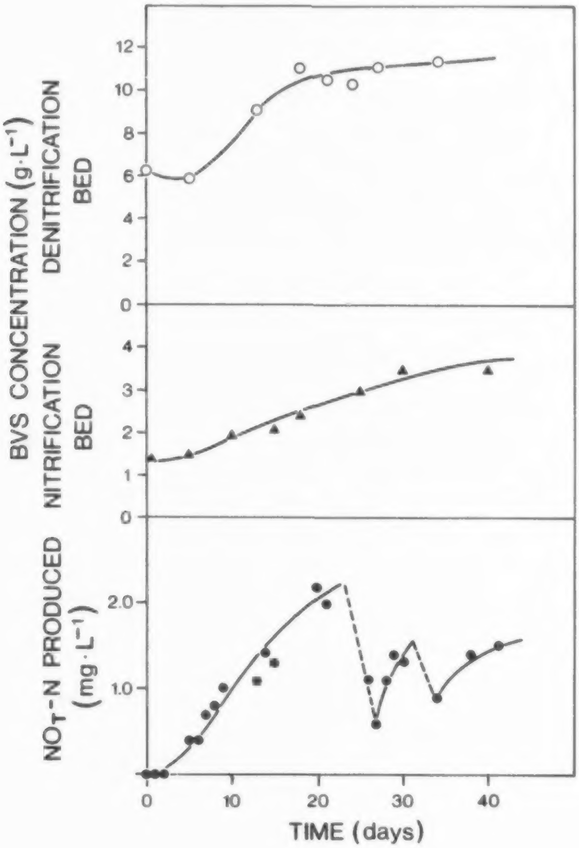

Figure 2. Start-up and Acclimation of the Fluidized Bed System.

The results of the pseudo-steady state runs are summarized in Table 3. It is evident from these data that, at the maximum loading investigated to date (Run 4), virtually complete oxidation of organic carbon and nitrogenous species was maintained by the coupled fluidized bed process. Total nitrogen removal efficiency during Run 4 was in excess of ninety percent. The treated effluent qualities for the pseudo-steady state runs are compared, in terms of FOC and NH_3-N concentrations, in Figures 3 and 4 respectively.

TABLE 2. PSEUDO-STEADY STATE OPERATING CONDITIONS

Run #	Anoxic Reactor HRT (h)	SRT (d)	Temp (°C)	pH	BVS (g·L^{-1})	Hyd. Flux* (m·min^{-1})	Recycle Ratio	Oxygenic Reactor HRT (h)	SRT (d)	Temp (C)	pH	BVS (g·L^{-1})	Hyd. Flux* (m·min^{-1})	Recycle Ratio	D.O. (mg·L^{-1})	System HRT (h)	SRT (d)
1	9.8	-	30-33	7.2	34.0	0.46	80	35.	-	30-33	7.4	4.3	0.82	540	4.6-5.5	44.8	230
2	4.8	17.5	26-30	7.3	27.7	0.57	100	35.	130.	26-30	7.1	7.0	0.88	580	4.3-6.0	39.8	41
3	3.2	30.0	27-31	7.3	23.6	0.59	67	23.3	110.	27-31	7.0	9.6	0.93	400	2.5-3.8	26.5	89
4	1.9	5.6	25-28	7.4	23.1	0.52	35	14.0	65.	25-28	7.1	12.1	0.60	154	2.8-3.8	15.9	20

* Hydraulic Flux defined as total volumetric flow per unit cross sectional area of reactor.

TABLE 3. PSEUDO-STEADY STATE PERFORMANCE OF TWO-STAGE BIOLOGICAL FLUIDIZED BED SYSTEM

Run #	HRT (hours)* Anoxic	Oxygenic	System		FOC	COD UF	COD F	Phenol	TKN UF	TKN F	NH_3-N	TCN	CNS	NO_3-N	NO_2-N	TN	SS
1	9.8	35.0	44.8	Effluent[1]	40.	270.	220.	0.08	9.0	7.5	1.0	4.5	1.8	0.0	2.5	11.5	[illegible]
				Removal (%)	95.1	91.1	92.2	>99.9	95.6	96.3	98.8	50.0	99.6	-	-	94.3	-
2	4.8	35.0	39.8	Effluent[2]	50.	428.	342.	0.15	13.3	11.8	2.4	3.8	1.8	0.4	1.0	14.7	[illegible]
				Removal (%)	94.3	87.6	89.9	>99.9	94.6	95.1	97.4	57.8	99.6	-	-	94.0	-
3	3.2	23.3	26.5	Effluent[3]	45.	355.	250.	0.17	9.8	8.8	0.4	6.2	1.6	0.0	1.8	11.6	[illegible]
				Removal (%)	94.1	89.1	91.3	>99.9	94.0	94.1	99.5	42.2	99.5	-	-	92.8	-
4	1.9	14.0	15.9	Effluent[4]	53.	335.	290.	0.14	11.4	10.5	0.3	7.0	2.3	1.6	1.0	14.0	[illegible]
				Removal (%)	93.7	90.1	91.0	>99.9	92.9	93.3	99.5	17.7	99.4	-	-	91.3	-

* Hydraulic retention time, based on empty bed reactor volume and coke waste feed rate.

[1] Median concentration, expressed in mg·L^{-1}, based on 9 consecutive days of pseudo-steady state operation.

[2] Median concentration, expressed in mg·L^{-1}, based on 23 consecutive days of pseudo-steady state operation.

[3] Median concentration, expressed in mg·L^{-1}, based on 16 consecutive days of pseudo-steady state operation.

[4] Median concentration, expressed in mg·L^{-1}, based on 21 consecutive days of pseudo-steady state operation.

TN - Total Nitrogen, TKN + NO_T-N
UF - Unfiltered
F - Filtered

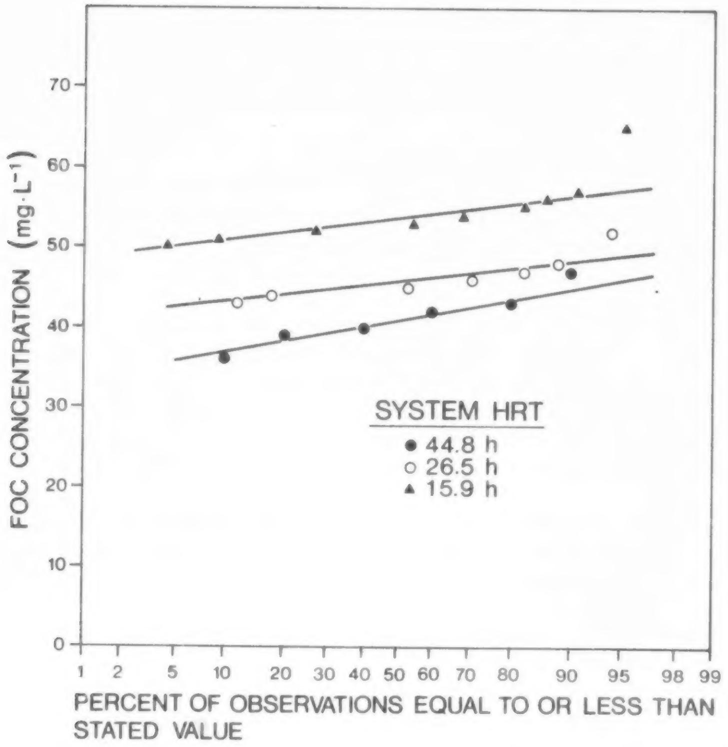

Figure 3. Effect of HRT on Treated Effluent FOC Content.

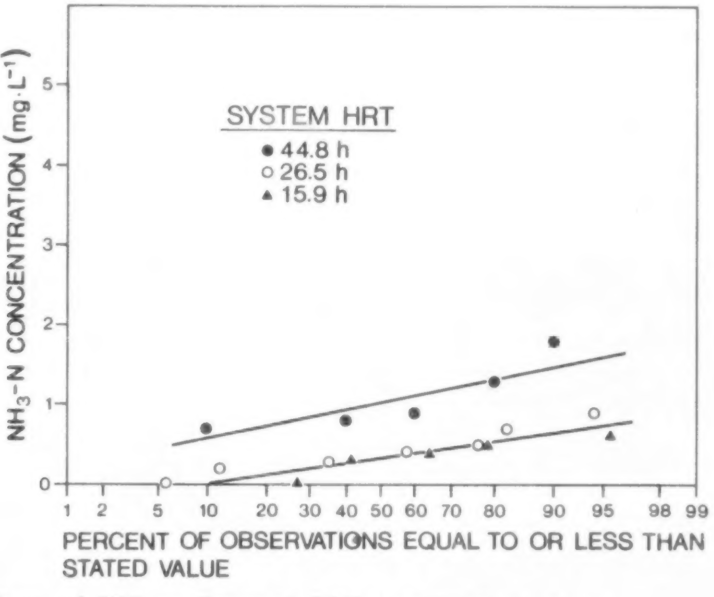

Figure 4. Effect of HRT on Treated Effluent NH_3N-Content.

The treated effluent FOC concentration has consistently been in the range of 35 to 70 mg·L^{-1} throughout the experimental program, representing a removal efficiency approaching 95 percent. The stable performance of the system in terms of carbon oxidation was unaffected by step changes in the process loading.

The maximum loading, in terms of the process nitrification capacity, has not been reached in the four pseudo-steady state runs. Effluent ammonia-N concentrations of less than 2 mg·L^{-1} were maintained despite the three-fold reduction in system HRT.

In all cases, inhibition of Nitrobacter was evident based on the incomplete conversion of ammonia to nitrate. This inhibition was also noted by Bridle et al (7) and several other researchers (4,5). The apparent deterioration in total cyanide removal efficiency between Run 1 and Run 4 may be due to changes in the relative quantities of free and combined cyanide in the raw wastewater as a result of long-term storage.

The effluent has consistently contained in excess of 50 mg·L^{-1} suspended solids and has averaged approximately 100 mg·L^{-1}. Mass balances and microbiological tests have not conclusively defined the source of these suspended solids; however, based on the nature of the biofilm in the two reactors, it would appear that they represent biomass from the nitrification system. The biofilms in the nitrification reactor have been less dense and considerably more dispersed than those in the denitrification reactor. Excessive losses of biomass from the fluidized bed biofilms have not been identified as a problem in any other industrial or municipal fluidized bed studies (19,20). Therefore, it is possible that the effluent quality will improve once true steady state has been attained in terms of the biofilm characteristics.

The conclusion of Bridle et al (7) with respect to suspended growth biological treatment of Dofasco coke plant wastewater was that complete nitrification and denitrification of full strength waste could only be achieved if low levels of powdered activated carbon (PAC) were added to the system. Furthermore, stable nitrification could not be maintained, even with PAC addition, at an aerobic HRT of 26 hours (1.1 days). A retention time of up to 48 hours in the nitrification reactor was necessary to ensure stable operation. Based on the pseudo-steady state results collected to date, the coupled fluidized bed process has been shown to provide a similar degree of treatment without PAC addition at a nitrification reactor HRT of sixteen hours or less. The ability to effect nitrification at increased volumetric loadings without PAC addition appears to be related to the high reactor biomass concentrations and the high SRT's which can be maintained in the nitrification reactor.

BIOFILM CHARACTERISTICS

As noted by other researchers who have studied fluidized bed denitrification systems (9), biomass concentrations approaching 40 g·L^{-1} could be readily attained in the denitrification reactor. Typically, the denitrification biofilms, during this study, were in the range of 100 to 200 μ in thickness. The establishment of active biofilms on the sand media allowed reduction in the fluidization flux from approximately 0.9 $m \cdot min^{-1}$ at start-up to an operating level of 0.5 $m \cdot min^{-1}$.

As the biomass concentration in the denitrification reactor increased, white deposits were noted within the biofilms. At the same time, the density of the biofilms increased significantly, requiring an increase in the hydraulic flux to the reactor to maintain adequate fluidization. Analyses of the biomass showed that calcium and phosphorus were accumulating within the biofilms. The progressive increase in BVS, calcium and phosphorus in the upper regions of the denitrification reactor is shown in Figure 5. At Day 0, the upper region of the denitrification reactor was poorly fluidized. An accumulation of white deposits was removed from this area of the reactor. Analyses of the biological material indicated high concentrations of calcium and phosphorus. Clean sand was added to the system to replace the media removed and the concentration of calcium and phosphorus in the upper region of the reactor monitored on a regular basis. After about fifty days of operation, the deposition of inorganic matter had again resulted in poor fluidization of the denitrification reactor. The calcium and phosphorus concentrations had reached the high levels noted prior to the addition of clean sand.

Based on analysis of the biofilms, the mass ratio of calcium to phosphorus was approximately 2.8, indicative of tetrabasic calcium phosphate ($4CaO \cdot P_2O_5$). X-Ray diffraction confirmed the presence of tetrabasic calcium phosphate in the biomass. The precipitation of tetrabasic calcium phosphate was also noted by Bridle _et al_ (7) during operation of suspended growth biological treatment units.

The accumulation of inorganics in the denitrification reactor did not appear to affect the biological treatment efficiency; however, the poor fluidization characteristics prevented adequate control of bed expansion and reactor SRT. Therefore, the biomass (BVS) concentration in the denitrification reactor has been maintained at approximately 25 $g \cdot L^{-1}$ to avoid excessive accumulation of inorganic matter.

The deposition of inorganic matter has also occurred in the nitrification reactor but at a lower level and has not adversely affected reactor operation; however, biomass concentrations equivalent to those maintained in the denitrification reactor have not been established in the nitrification system. Previous investigations (19) of fluidized bed nitrification of municipal secondary effluent showed that establishing high concentrations of biomass was a limiting factor in attaining high volumetric conversion rates. A similar problem was identified during this investigation.

Figure 6 shows the concentration of biomass in the nitrification reactor since start-up in June 1980. After the acclimation period and subsequent to restabilization of the process following a severe pH shock, the biomass concentration in the nitrification reactor reached an equilibrium level of approximately 4.5 $g \cdot L^{-1}$. The biofilms were extremely thin, in the range of 50 to 60 μ. Hydraulic fluxes in the range of 0.9 to 1.0 $m \cdot min^{-1}$ were necessary to maintain fluidization as the biofilms were not sufficiently thick to affect significantly the overall particle density. These high hydraulic loadings created excessive turbulence in the reactor, preventing the establishment of high biomass concentrations.

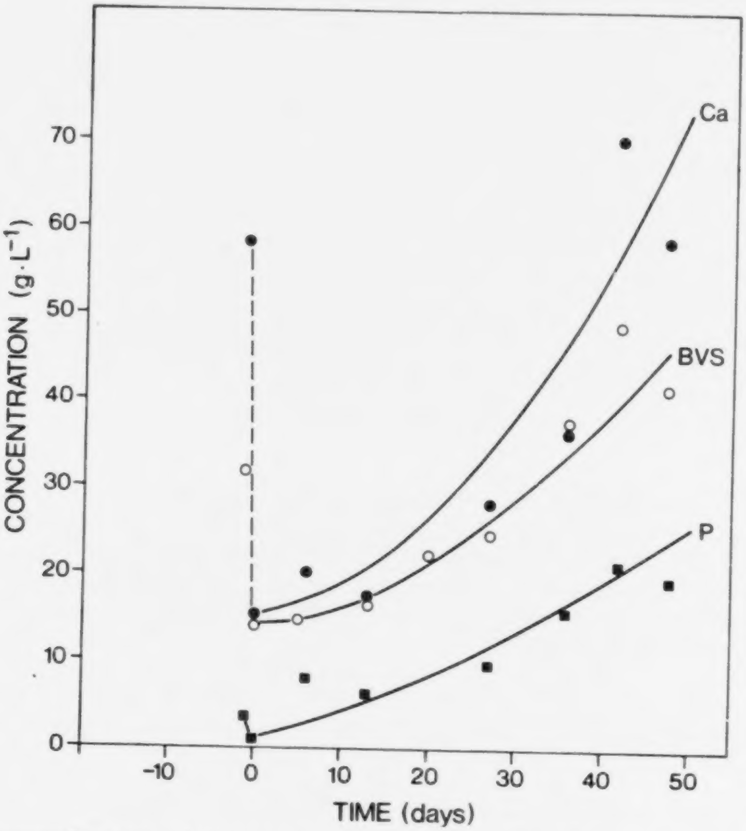

Figure 5. Accumulation of Biomass, Calcium and Phosphorus in the Denitrification Reactor.

The original reactor design included a conical entrance to the column and up-flow entry of the feed stream. Based on discussions with Dorr-Oliver, the inlet piping was redesigned such that the feed entered vertically downward into the apex of the cone. As evident from Figure 6, there was a slight increase in the concentration of biological matter in the reactor; however, the biomass concentration appeared to stabilize at approximately 5.5 $g \cdot L^{-1}$. Therefore, a perforated distribution plate was designed for the reactor and the inlet piping restored to the original up-flow configuration. The plate distributor was installed on Day 233 of operation. In retrospect, according to Figure 6, the down-flow distribution system may have produced the same result as the perforated plate. The nitrification reactor BVS concentration increased to approximately 13 $g \cdot L^{-1}$ over the next hundred days of operation. At this time, the plate was removed since plugging had become evident. The hydraulic flux on the nitrification reactor was gradually decreased to an operating level of 0.5 $m \cdot min^{-1}$ and removal of the distribution plate at the reduced turbulence level did not adversely affect the system.

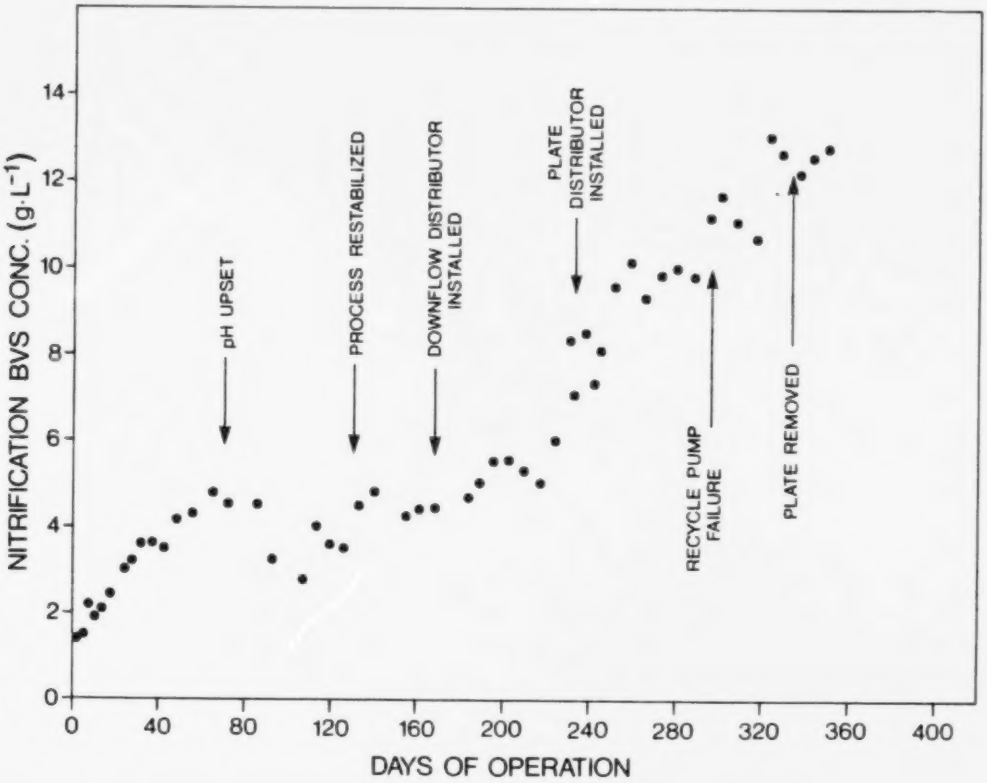

Figure 6. Biomass Concentration in the Nitrification Reactor.

On the 296th day of operation, as shown in Figure 6, the main recycle pump failed, causing the beds to settle. Approximately six hours of maintenance was required to remedy the problem, during which there was no flow through the reactors. At start-up, the turbulence created during fluidization sheared some biomass from the nitrification reactor; however, the losses were minimal and had little effect on the process.

SUPPLEMENTAL CHEMICAL REQUIREMENTS

The pre-denitrification flow configuration reduces the requirement for supplemental carbon addition by utilizing the raw waste components as the carbon source for the denitrification reactions. Bridle et al (6) established that complete denitrification of Dofasco coke plant wastewater required a feed FOC/TN ratio in excess of 3.5. The raw wastewater used during the pseudo-steady state investigations fulfilled this requirement and no supplemental carbon addition was necessary.

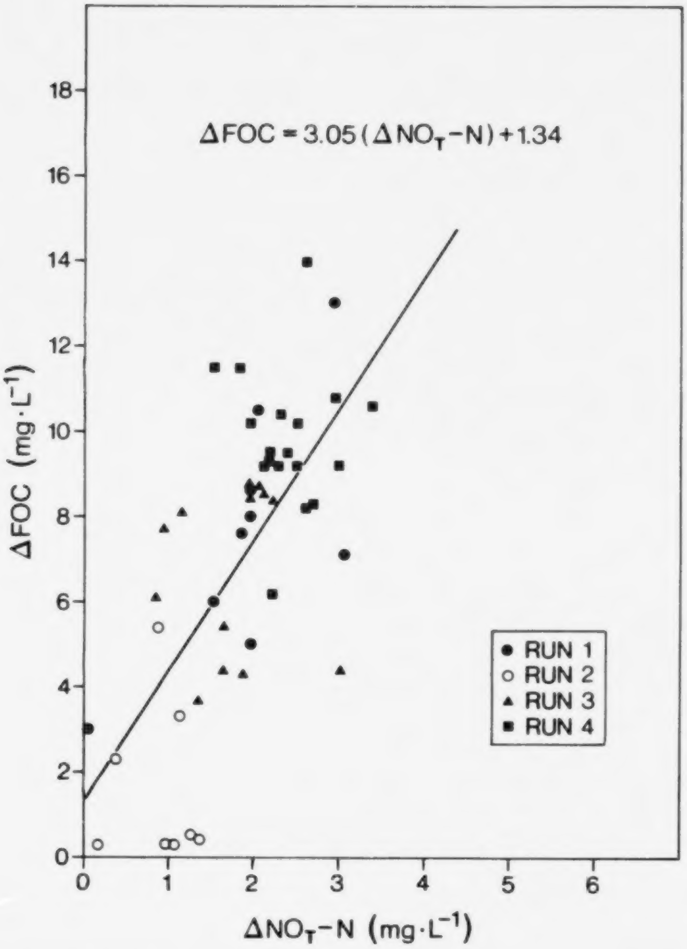

Figure 7. Relationship Between FOC and NO_T-N Removal in the Denitrification Reactor.

The data presented in Figure 7 show the relationship between organic carbon removed in the denitrification reactor and the removal of oxidized nitrogen species (nitrate and nitrite). The denitrification reactor was responsible for the removal of approximately 3 mg FOC per mg NO_T-N removed. The pre-denitrification operating mode significantly reduces the oxygen requirements of the oxygenic nitrification reactor by the removal, under anoxic conditions, of a considerable fraction of the feed organic carbon content.

The phosphorus demand of the wastewater ranged from approximately 50 mg P per litre of coke plant effluent treated to 170 mg P per litre treated. As discussed, a fraction of the phosphorus demand was related to the precipitation of calcium phosphate. In the biological treatment of coke plant wastewater from a fixed ammonia still operated using sodium hydroxide pH adjustment, Medwith and Lefelhocz (8) supplemented the feed with 40 to 70 mg P per litre of wastewater treated.

CONCLUSIONS

Based on the preliminary results of the on-going investigation of two-stage treatment of coke plant wastewater using the fluidized bed process, the following conclusions can be drawn:

- The fluidized bed process is capable of achieving complete nitrification and denitrification of undiluted coke plant wastewater without the addition of powdered activated carbon to the system. Total nitrogen removal efficiencies in excess of 90 percent could be maintained in the fluidized bed process at a total system HRT of 16 hours. In a suspended growth system treating a similar wastewater, a system HRT of up to 60 hours and the addition of low levels of PAC were necessary to attain the same degree of treatment.

- The pre-denitrification flow configuration significantly reduces the oxygen requirements of the nitrification reactor. Mass balances around the denitrification reactor indicated the anoxic removal of approximately 3 parts of organic carbon per part of oxidized nitrogen removed.

- Biomass concentrations up to 40 $g \cdot L^{-1}$ were achieved in the denitrification reactor; however, operational concentrations are limited to approximately 25 $g \cdot L^{-1}$ due to the accumulation of inorganic deposits of tetrabasic calcium phosphate in the biofilms.

- Flow distribution appears to be a critical factor in achieving high biomass concentrations in the nitrification stage of the coupled fluidized bed process. Once improvements were made to the oxygenic reactor design, biomass concentrations up to approximately 15 $mg \cdot L^{-1}$ were achievable. Excessive turbulence does not appear to be as significant a factor in the establishment of biofilms in the denitrification system.

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TRACE METAL REMOVAL
FROM STEEL PLANT WASTEWATERS
USING LIME AND FERRATE

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ABSTRACT

Trace metals (zinc, cadmium and lead) and suspended solids (clays and biological flocs) were removed from simulated and actual Steel Plant wastewaters (scrubber water blowdown from BOF and blast furnance and coke plant lime still and secondary biological effluent) using treatment with 1) lime followed by potassium ferrate (K_2FeO_4), 2) ferrate only and 3) ferric chloride only. Results show that ferrate can achieve very high cadmium removal following lime treatment. Ferrate treatment alone on simulated scrubbing waters can remove Cd and Pb better or poorer than ferric depending principally on solution pH. Biological solids effectively scavenge metals such as lead, zinc and cadmium in the treatment of coke plant biological wastewaters. If settling of biological solids is inefficient, ferrate can coagulate the suspended solids and associated trace metals, although high doses are required.

INTRODUCTION

USEPA pretreatment guidelines for industrial waste discharge as well as wastewater treatment authority ordinances have pushed the burden of pretreatment of industrial wastewaters particularly those containing toxic heavy metals to treatment at their source. Economic and regulatory motives then exist for pretreatment of metal bearing wastewaters of a wide variety to minimize carriage into publicly owned treatment works (POTW). Often, metals are removable in POTW's but contaminate waste sludges, thereby limiting their utility as an agricultural resource.

Pretreatment techniques such as precipitation, oxidation and adsorption have been proposed for a variety of steel industry wastewaters. In this work, focus is on a novel form of iron (ferrate) as the treatment reagent to remove trace metals and suspended solids from steel industry wastewaters, particularly those from blast furnace gas cleaning and coke production. This

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work attempts to refine and extend earlier effort (1, 2) where ferrate was reported to have good oxidation/coagulant properties.

The work herein describes some behavior of ferrate in terms of suspended solids and trace metal removal on both well defined solutions and actual wastewaters. Combinations of lime pretreatment and ferrate postreatment as well as ferrate and ferric treatments alone are used. The experimental system employed utilized bench scale jar tests to examine feasibility of ferrate treatment as well as obtain possible mechanistic insights into trace metal removal processes. Equilibrium chemistry model calculations are compared to experiment in an attempt to generalize results.

THEORY

Since this was an exploratory research project, jar tests were employed as the major experimental tool. Such tests simulate unit operations of rapid mixing, flocculation, gravity settling and granular filtration if supernatant is filtered. Major removal mechanisms include adsorption/coprecipitation, flocculation, settling and possibly filtration and the sequence of occurrence are schematized on Fig. 1. Whatever the removal mechanisms are, a full scale process design cannot be directly scaled from far test results, although such results are widely used as a major element in design.

In the coagulation process, K_2FeO_4 reacts in water to produce probably amorphous ferric hydroxide floc particles ($Fe(OH)_3$). A simplified expression of this reaction is:

$$\begin{array}{lll} Fe^{+6} \ +3e^{-} & \longrightarrow Fe^{+3} \ +3\ OH^{-} & \longrightarrow Fe(OH)_3 \downarrow \\ \text{(purple color} & \text{(yellow or} & \text{(white} \\ \text{in solution)} & \text{colorless solution)} & \text{precipitate)} \end{array}$$

As shown, the reaction actually has two steps: The first is an oxidation-reduction reaction in which the Fe^{+6} from the FeO_4^{-2} ion oxidizes water and/or other reduced species present; the iron in turn is reduced to Fe^{+3}. The second reaction is a hydrolysis (ligand exchange) reaction in which the Fe^{+3} coordinates effectively with three OH^- ions to form $Fe(OH)_3$ solid phase particles (and other, soluble hydrolysis products).

The slow stirring in the second phase of the jar test promotes inter-particle collisions. Some fraction of these collisions result in lasting contact and particle (floc) growth. Eventually, particles large enough to settle out in the 30 minute settling period of the test are formed.

Leckie et al (3) examined the removal of trace metals by adsorption/coprecipitation on aquo ferric precipitates. Ferric oxy hydroxide is the common form of iron generated in either coprecipitation where iron is added to a trace metal solution or in precipitate adsorption/scavenging where it is preformed, then added to the trace metal solution. If the trace metal exists at very low concentrations (insufficient to generate sufficient extensive colloidal precipitates) the general removal extent for cations by adsorption on ferric oxy hydroxide is a sigmoidal function of pH. The position of the

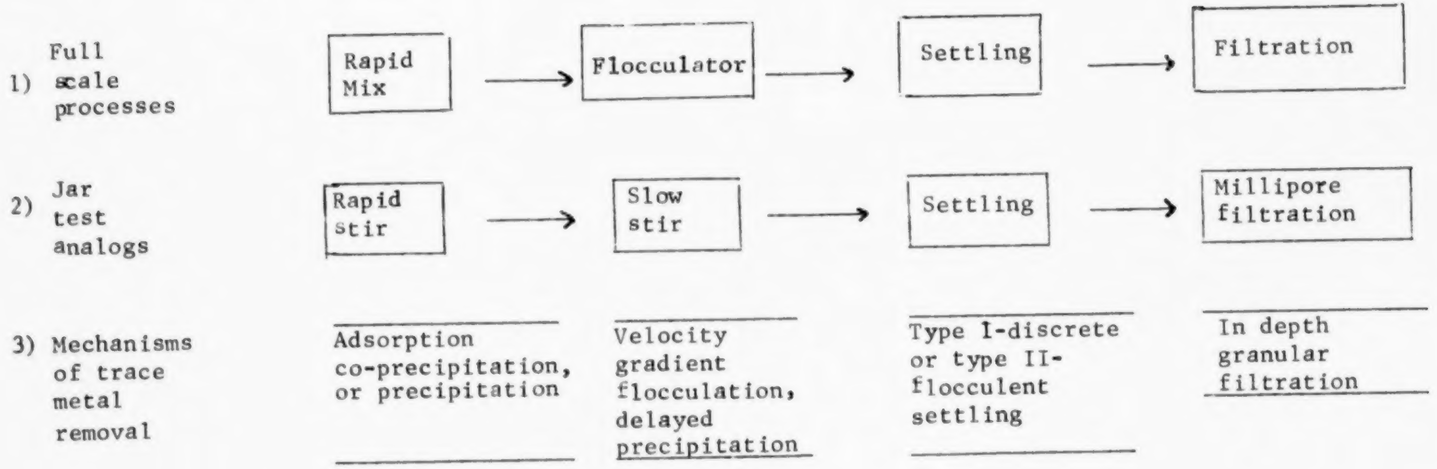
1) Full scale processes
Rapid Mix
Flocculator
Settling
Filtration
2) Jar test analogs
Rapid stir
Slow stir
Settling
Millipore filtration
3) Mechanisms of trace metal removal
Adsorption co-precipitation, or precipitation
Velocity gradient flocculation, delayed precipitation
Type I-discrete or type II-flocculent settling
In depth granular filtration

Figure 1. Schematic of Sequential Treatment Processes and Removal Mechanisms

sigmoidal adsorption edge (see Fig. 2) is a function of the particular trace metal concerned, its initial concentration, and to a certain extent the concentration of competing ligands. It was concluded (3) that coprecipitation or adsorption steps are very fast compared to typical process times and thus not rate limiting.

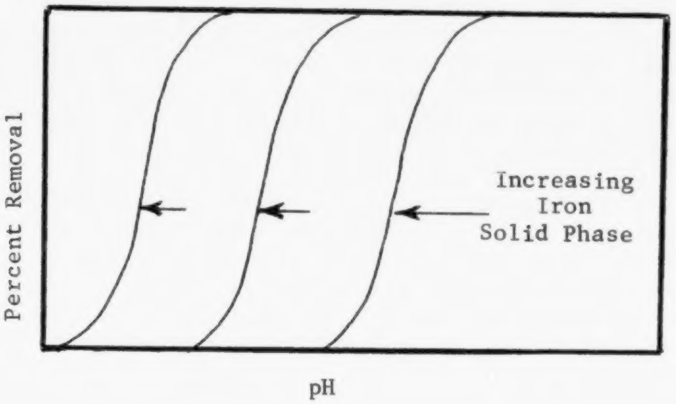

FIGURE 2. Trace metal adsorption behavior on iron hydrous oxide.

However, when the trace metal exists, at higher concentrations and can form a colloidal precipitate, i.e. as a carbonate, hydroxide or mixed hydroxy carbonate, the removal is likely to be governed by hererocoagulation between the forming colloidal $Fe(OH)_3$ and the trace metal colloid, both of whose surface charges may vary as different functions of pH. Thus, as pH is lowered, rapidly forming $Fe(OH)_3$ coagulates trace metal colloids at pH values where both surface charges diminish, approaching their zero point of charge (ZPC). However, at high pH, the removal is hindered by the fact that the net charge on both the iron and trace metal colloids grow more negative leading to mutual repulsion. Thus only weakly or partially destabilized colloids aggregate slowly and not extensively enough to permit rapid sedimentation and separation without filtration.

If lime is used in pretreatment, the trace metal is removed as a carbonate or hydroxide precipitate in the sweep $CaCO_3$ floc formed. Residual trace metal not removed in these steps could be removed by decreasing pH and using post ferrate addition. The post ferrate treatment should be qualitatively the same as without lime pretreatment if the solution chemistry is similar.

A complete theoretical framework for interpreting results is unavailable for either model or even actual wastewaters; in modal experiments, initial concentrations of trace metals is high enough that colloidal rather than dissolved metals occur and thus coagulation/destabilization rate processes may govern the removal but are only poorly understood. In actual wastewaters, the existence of added complexing ligands, surfactants, emulsions, etc., are not simulated by corresponding theory and agreement between model and actual wastewaters may only be qualitative at best. Further interpretation of results presented here is developed elsewhere (4).

EXPERIMENTAL

Experiments consisted of a series of model studies with jar tests followed by treatment of actual steel plant wastewaters. Lime alone, lime plus ferrate, ferrate alone and ferric chloride alone were employed in separate tests to remove initial concentrations of Cr(VI), Pb(II), Cd(II) and Zn(II) that ranged from 0.2 to 5 mg/l. Solution chemistry was varied in the model as well as actual wastewater treatment schemes. The major independent variables were pH and coagulant dose. Alkalinity and sulfate were the major anionic species controlled in the model tests. Test conditions are divided into four phases as shown on Table 1 where the order of the phase is not necessarily chronological.

Sequence of testing included finding the optimum lime dose on waters that might chemically mimic some of those found in an integrated steel mill (Phase IA). Then post lime treatment with ferrate would be employed to "polish" the effluent and remove trace metals to a very low level. This procedure was repeated on actual steel plant wastewaters in Phase IB. Phase II provided data on ferrate only treatment of Lake Michigan water spiked with several trace metals (Cr, Pb and Cd). Phase III compared ferric and ferrate behavior under independent variation of solution pH, Fe dose and initial concentration of alkalinity, sulfate and thiocyanide in an attempt to bracket some background chemical conditions found in steel plant wastewaters. Phase IV examined utility of ferrate to remove Cd and Zn from actual steel mill wastewaters. In Phase IB waters were not spiked with any trace metals.

Jar test procedures used for all study phases employed essentially similar conditions: Rapid mixing at 100 to 120 RPM for 1 minute followed by slow mixing at 30 to 50 RPM for 20 minutes, followed by quiescent settling for 30 to 60 minutes. At the conclusion of the test, samples were siphoned off and some millipore filtered (0.22μm or 0.45μm) and analyzed for residual trace metal by atomic absorbtion spectrometry or γ-ray spectroscopy when radioisotopes of trace metals were employed. The schematic diagram of the jar test experiments is shown in Fig. 3. Exact experimental procedures employed and individual test equipment is described elsewhere (4, 5, 6).

RESULTS

The presentation of results encompasses the four phases outlined on table 1. Chronological sequence of phases was: II, IA, IB, III, IV. In addition, other efforts to better determine the colloid chemical behavior of ferrate in water, coagulation of kaolinite, bentonite and polystyrene latex were essentially run in parallel with phase II.

Phase IA results are presented in greater detail elsewhere (5) but nevertheless show that for independent variation of initial concentrations of cadmium, sulfate and alkalinity, optimum cadmium removal from solution occurred at anywhere from 90 to 1500 mg/l of lime, (as $Ca(OH)_2$) as shown on table 2. These optimum treated waters had the same as initial sulfate but drastically reduced alkalinity and roughly 60% removal of cadmium. Large batches of each initial water was lime treated at its optimum, then adjusted to pH 7, 8, or 9 and post treated with ferrate at fixed dose and fixed pH. Representative results are in figure 4A and 4B for two conditions:

TABLE 1. EXPERIMENTAL CONDITIONS

Test	Chemical and Dose Range				Water			Trace Metal			
	Lime	Ferrate		Ferric							
	Pretreat	alone	post treat	alone	model	natural	wastewater	Cd	Pb	Zn	Cr
IA	X				X			X			
	X		1.5 - 20*		X			X			
IB	X						X	X	X	X	
	X		1.5 - 12				X	X			
II		0.5 - 10				X		X	X		X
III		5 - 40			X			X	X	X	
				5-40*	X			X	X	X	
IV		10 -100					X	X		X	

* denotes dose range of Fe compound (mg/l as Fe).

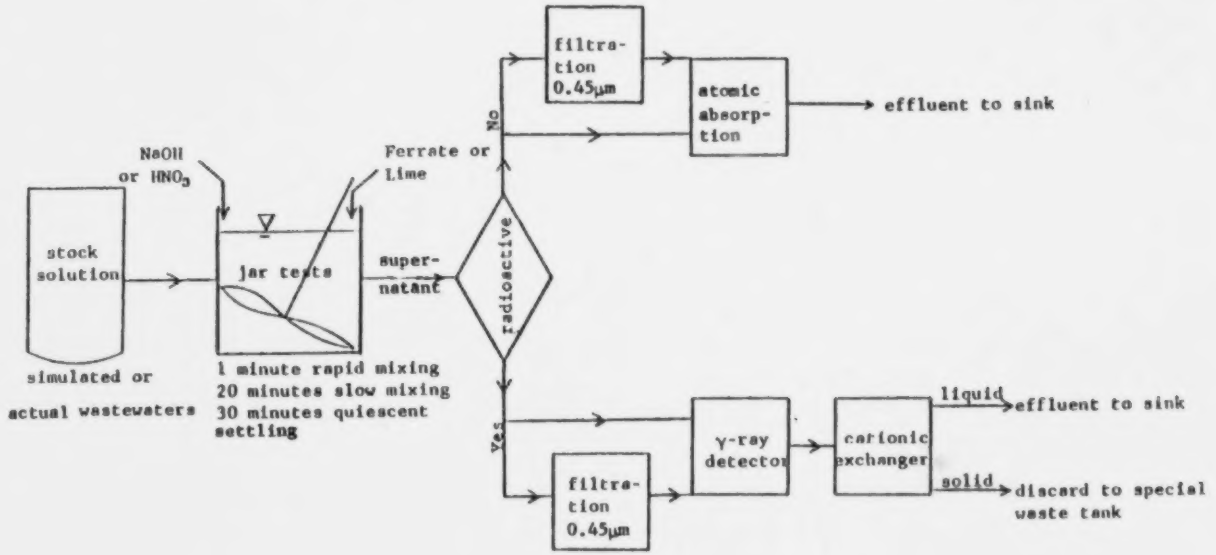
stock solution
simulated or actual wastewaters
NaOH or HNO_3
jar tests
Ferrate or Lime
1 minute rapid mixing
20 minutes slow mixing
30 minutes quiescent settling
super-natant
radioactive
No
Yes
filtration 0.45μm
atomic absorption
effluent to sink
filtration 0.45μm
γ-ray detector
cationic exchanger
liquid
effluent to sink
solid
discard to special waste tank

Figure 3. Schematic Diagram of Jar Test Study

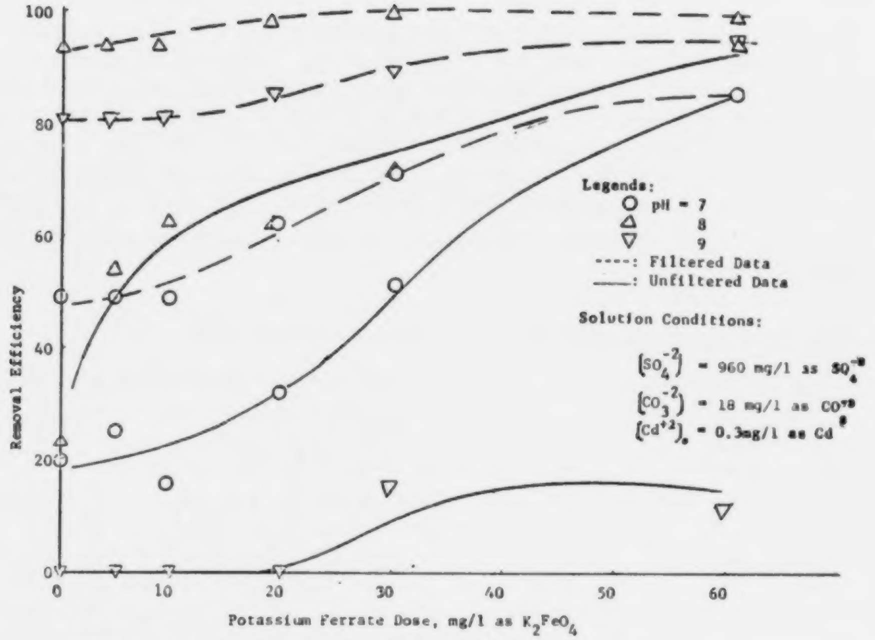

FIGURE 4-A. Ferrate Post Treatment of High Ionic Strength Water

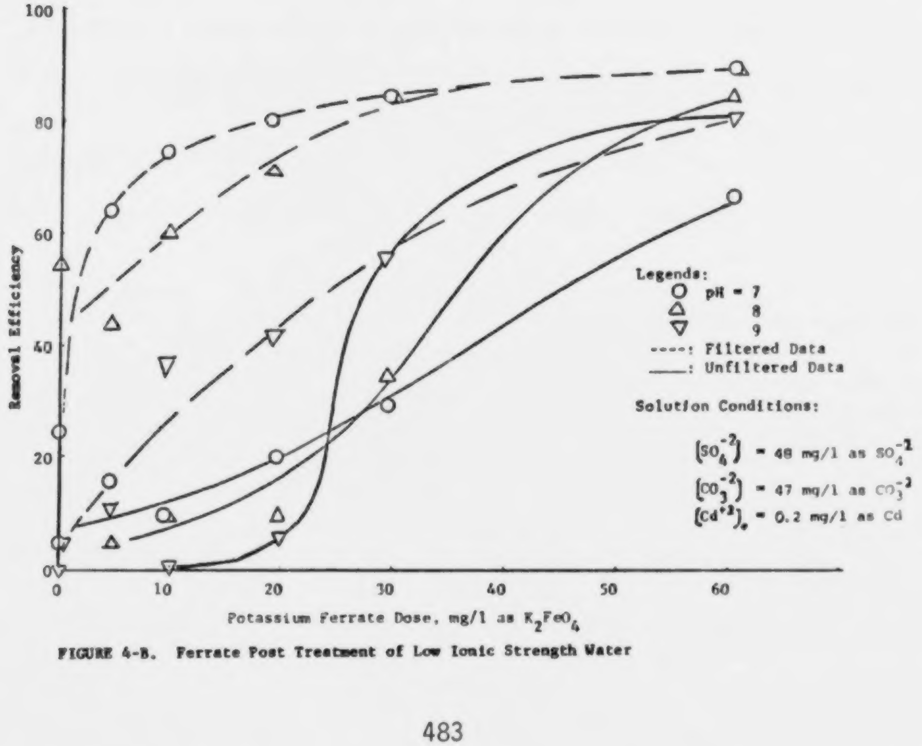

FIGURE 4-B. Ferrate Post Treatment of Low Ionic Strength Water

one with high ionic strength (due to SO_4^{-2}) and one with low $[SO_4^{-2}]$. These show significantly different behavior with and without post filtration. With post filtration, higher removal efficiency is observed with the high ionic strength case at all doses and pH≥8 whereas low ionic strength waters showed considerable improvement in removal efficiency only at low dose and pH≤8. Monotonic increase in removal is observed for all but the case with high (5 mg/l) initial cadmium but low sulfate and alkalinity where optima of 5 mg/l K_2FeO_4 and 30 mg/l K_2FeO_4 were observed at pH=8 and 7, respectively. These complex patterns were displayed for other solution conditions and are discussed later.

TABLE 2. Lime pretreatment solution conditions (Phase IA)

series	$[SO_4^{-2}]$	$[C_T]$ #	$[Ca^{+2}]$	$[Cd^{+2}]$	Lime mg/l
1	48	305 (25)	(10)	5 (2)	90
2	1920	1220 (44)	(11)	5 (~2)	150
3	1920	1220		0.5 (0.32)	1500
4	960	610 (18)	(11)	5 (0.32)	740
5	48	305 (47)	(10)	0.5 (0.2)	200

* Bracketed items are concentrations after lime pretreatment.
** Lime dose is "optimum" based on marginal utility of less than 0.17 % removal increase/mg/l dose increase
*** All concentrations are mg/l as the ion, and Lime is as $Ca(OH)_2$.

# C_T is total alkalinity (carbonate form at pH following lime pretreatment).

Phase II results are presented elsewhere (4) due to space limitation here and the fact that they focused on a natural water. Those results show that Cr is not appreciably removed unless reduced to the +3 oxidation state as has been shown by Sorg (7). However, Cd (II) and Pb (II) require no oxidation or reduction for removal. For high initial concentration (~5mg/l) Cd and Pb removal is an increasing function of pH with >95% lead removal at as little as 7 mg/l K_2FeO_4 (as Fe) at optimum pH between 7 and 8. For cadmium, up to 20 mg/l K_2FeO_4 (as Fe) can only remove 80-90% of original cadmium at the optimum pH=9. These along with Phase III results provide a basis for generalizing the interpretation of Cd, Pb and Zn removal from selected steel plant wastewaters.

Phase III allows us to gain some insight into how a few solution conditions affect trace metal removal, in well defined laboratory systems. Type and concentration of Fe coagulant, solution pH, ionic strength, and sulfate and thiocyanide concentrations are independently varied. Thiocyanide rather than thiocyanate was chosen because cyanide has carbon at a lower oxidation state than cyanate and ferrate may oxidize it somewhat in the process of removing the heavy metals (8). Ferric iron added as $FeCl_3$ on the other hand should show no such reaction. Process wastewaters may be pretreated by lime; solution chemistry reflecting this was also examined in Phase III. A solution condition of 4×10^{-3} eq./l alkalinity, 20 mg/l sulfate and zero thiocyanide was standard. Initial solution pH was equilibrated in batches at from 6.5 to 9.5 prior to dosing with potassium ferrate or ferric chloride at from 5-40 mg/l (as Fe).

Some of the more salient results for cadmium, zinc and lead removal by ferrate and ferric are shown in Figs. 5, 6 and 7 respectively. More detailed results are also available elsewhere (6). Cadmium and zinc behave similarly; both show rapid increase in removal with increasing pH up to 8. Thereafter, behavior is different for each coagulant; at a high dose (40 mg/l as Fe), ferrate induced removal decreases from a 90% maximum at pH = 8 while ferric generated removal plateaus at 95% at pH>8. At lower doses ferrate shows a minimum removal at pH = 8 that is significantly less than for ferric. In both cases at pH = 9, considerable removal (70% for Zn and 50% for Cd) is attributed to precipitation induced removal alone. Both ferric and ferrate removed lead more efficiently at lower doses and especially at lower pH than cadmium or zinc. As little as 5 mg/l of Fe (III) removed an average of 85% Pb over the pH range of 7 to 9 while even 40 mg/l Fe (VI) would not achieve this unless pH < 8.

The three trace metals Pb, Cd and Zn were generally removed better by $FeCl_3$ than K_2FeO_4. The difference in removal almost disappears when jar test supernatatant is filtered. This is most true for zinc and for all three metals at pH < 8. Furthermore, comparable experiments at ionic strength up to 0.05, sulfate to 2000 mg/l and thiocyanide to 100 mg/l showed only a slight diminution (< 15%) in removal. This only occurred around 15 mg/l ferrate (as Fe) and at no other dose up to 40 mg/l.

Actual wastewaters from a local Chicago steelmaking plant were tested in Phases IB and IV. Wastewater streams from basic oxygen furnace (BOF), blast furnace, hot and cold rolling, acid pickling and cokemaking were sampled and analyzed on three occasions for trace metal and other parameters. These analyses guided selection of solution conditions for model tests in Phases IA and III and evaluated the wastewaters most amenable to ferrate treatment. Details of this are also presented elsewhere (4). Finally, two wastewater streams with potential and need for treatment to remove trace metals were chosen: blast furnace scrubber blowdown and coke plant wastewater. The former is a moderate volume waste stream that may be discharged while the latter requires considerable treatment to remove organics and ammonia before discharge. In both waters, ambient levels of most trace metals including Pb and Cd were in the 0.05 mg/l range and were largely not pursued. Zinc existed in the 1.0 mg/l range in all blast furnace blowdown samples and was given greatest attention in terms of direct measurement in laboratory treatment tests.

Wastewaters were treated with both lime (pretreatment) and ferrate (post treatment) in Phase IB and ferrate only treatment in Phase III. Considerable lime dose (1500 mg/l) was required to remove zinc in BF blowdown from

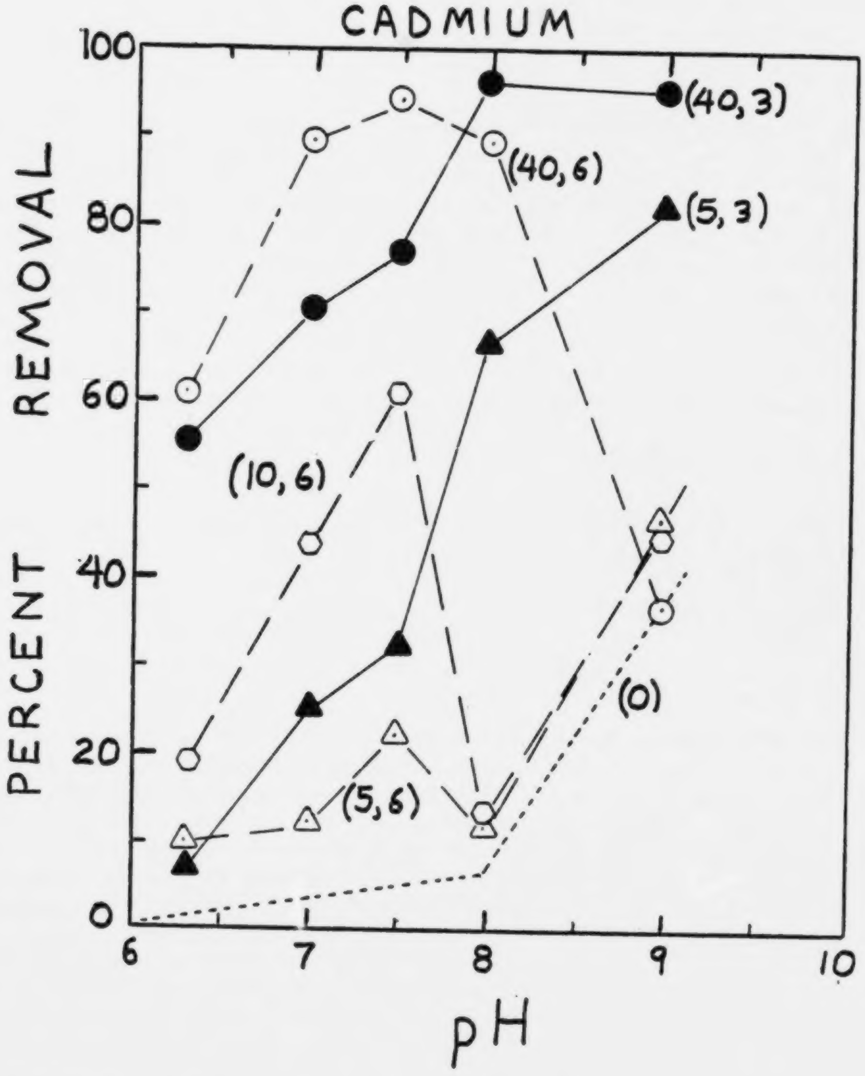

FIGURE 5. Cadmium removal vs. pH for fixed dose of ferric (III) and ferrate (VI). Dose and oxidation state, 3 or 6 of coagulant is indicated as pairs e.g. (40,6) is ferrate at 40mg/ℓ as Fe. Removal by pH adjustment alone is the (0) curve.

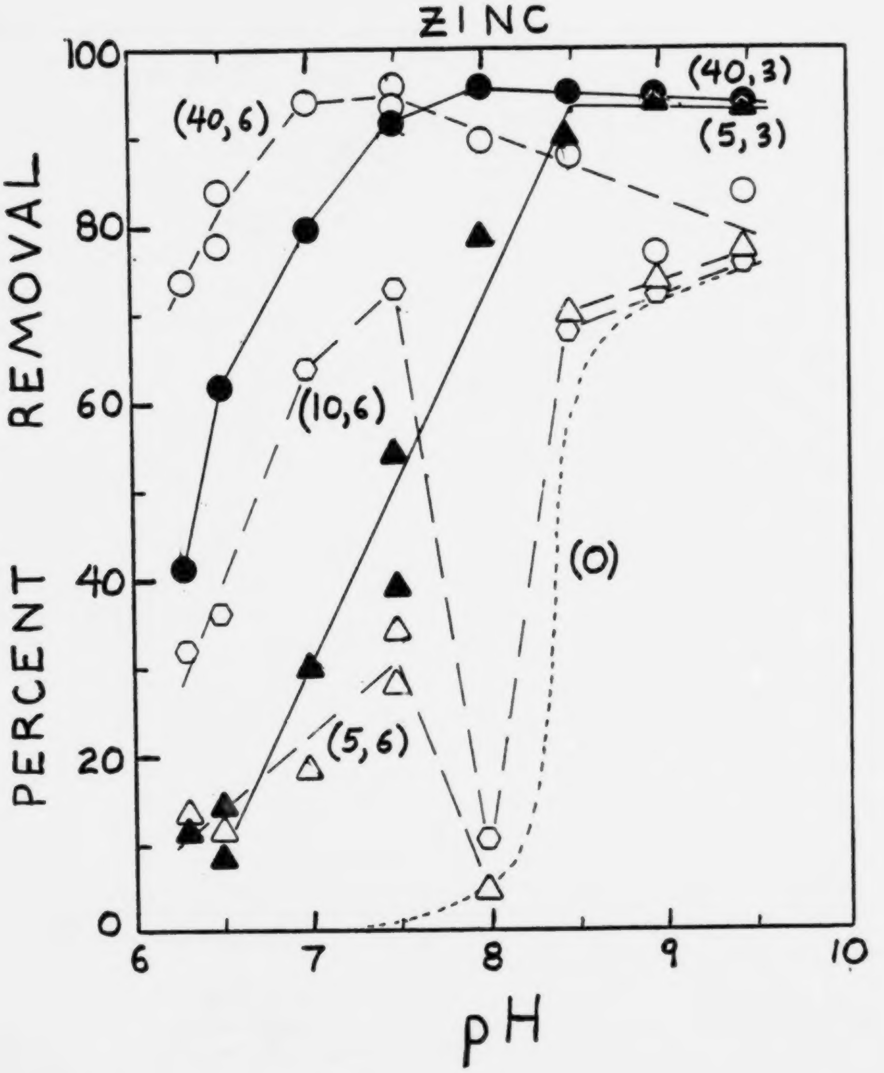

FIGURE 6: Zinc removal vs. pH for fixed dose of Fe(III) and Fe(VI). Same comments as figure 5.

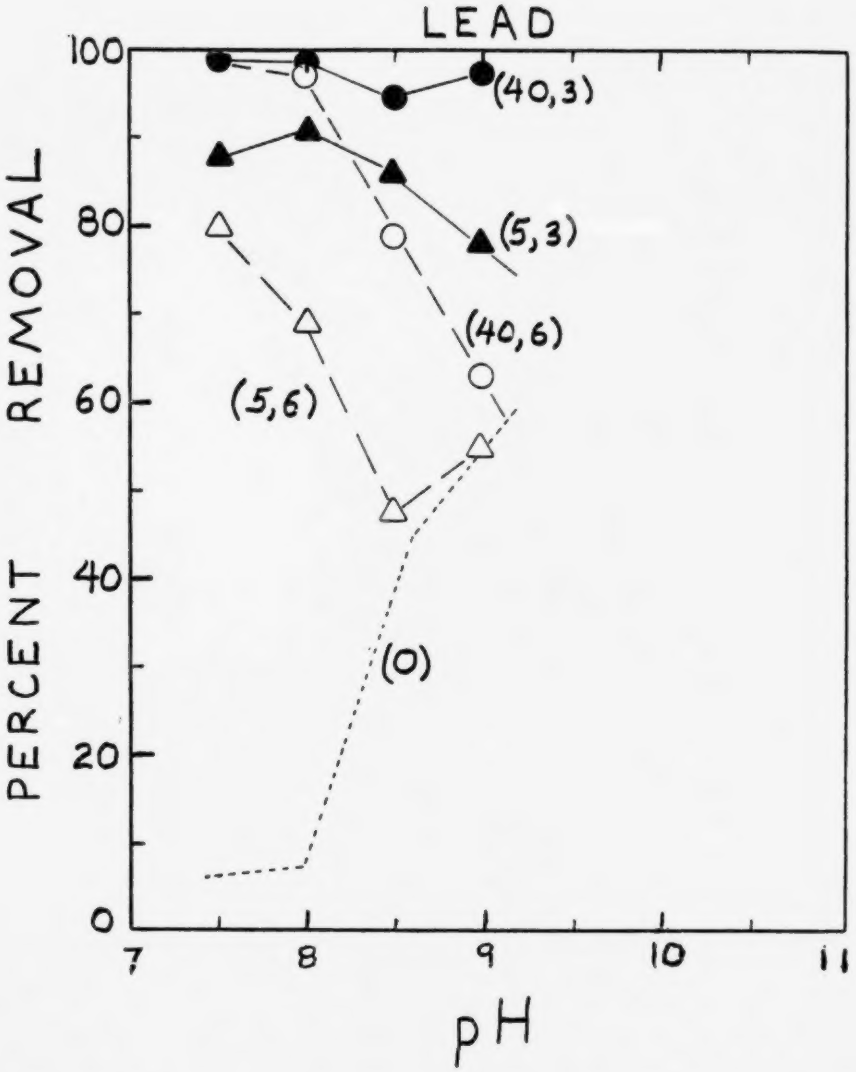

FIGURE 7: Lead removal vs. pH for fixed dose of Fe(III) and Fe(VI). Same comments as figure 5.

1.1 mg/l to 0.15 mg/l but none was required for BOF and cokemaking secondary treated wastewater with initially 0.06 mg/l and 0.03 mg/l zinc, respectively. With virtually no lime addition these latter wastewater concentrations were reduced to analytical detection limits. Pretreatment of BF blowdown with 150 mg/l lime resulted in 0.7 mg/l residual zinc at pH~8 and only 1.5 mg/l ferrate (as Fe) post treatment was required to achieve 0.05 mg/l residual Zn.

An additional set of samples was obtained to measure the matrix effects of wastewater constituents on trace metal removal. Samples of ammonia lime still effluent from a coking operation both before (1) and after (2) activated sludge treatment and a blast furnace scrubber blowdown (3) were spiked with labelled Zn_{65} to 1.0 mg/l and Cd_{109} to 0.5 mg/l. Wastewater samples were adjusted to pH = 7.5-8.0 and dosed with 0-100 mg/l (as Fe) ferrate; results are given in Table 3 in the order of samples 1, 2 and 3. In the upper part of the table, pH adjustment alone shows large removal of trace metals. The lower part of the table shows that after pH adjustment residual Cd and Zn may vary considerably. Then with increasing dose of ferrate at fixed pH, trace metal removal also monotonically increases. Sample 3 requires least and sample 1 the greatest dose to achieve a 50% removal percentage for both Cd and Zn. Samples 1 and 3 also show closely parallel removal of Cd and Zn with dose suggesting that removal is closely related to the fact that the added trace metal is associated with a solid phase at time of ferrate dosing. For comparison, bracketed values on Table 3 show that post lime treatment by ferrate at as little as 1.5 mg/l as Fe would remove 76% of total zinc in an actual wastewater sample. This compares closely to the steep dose-response relationship observed for the spiked BF blowdown sample.

DISCUSSION

Experimental results from Phases IA and III were compared to calculations using REDEQL/II (9), a computer code for determining chemical equilibrium in heterogeneous natural or simulated waters. REDEQL provides for precipitation of solid phases of trace metals and adsorption of soluble trace metals. Theoretical calculations for Phase IA significantly overpredict observed results at any pH. For Phase III, the qualitative trend of a sigmoidal adsorption edge (cf. Fig. 2) is predicted for Cd and Zn, but shows little dependence on ferrate dose. Results presented in Figs. 5 and 6 show portions of such sigmoidal curves with a strong dependence of position on dose. The reason for this discrepancy is not clear, but could be that the process is kinetically controlled. REDEQL/II results for lead agree better with experiments showing qualitatively that removal should peak at about pH = 8. Theoretical prediction in that case still underpredicts observed removal. The overriding observation from all the REDEQL calculations is that dose effects are more poorly predicted than pH effects. One conclusion is that more attention to rate processes is required if model calculations are to have wider utility and predictability.

Model wastewaters (well defined chemistry) and actual steel plant wastewaters are most similar for blast furnace blowdown and show good correlation, cf. Figs. 5 and 6 and Table 3. When suspended solids exist in the actual wastewater, high removal of trace metals by ferrate or ferric must be paralleled by high suspended solids removal. Ferrate reaction at high pH

TABLE 3. Percent Removal of Cd and Zn from Three Wastewaters

SOURCE	DOSE mg/l as Fe	(1) LIME STILL		(2) LIME STILL (After secondary treatment)		(3) B.F. BLOWDOWN	
Trace metal		Cd	Zn	Cd	Zn	Cd	Zn
Trace metal initial conc.		0.5	1.0	0.5	1.0	0.5	1.0 (0.7)**
Conc. after pH adjust to 7.5 - 8.0		0.075	0.035	0.43	0.87	0.06	0.29 (0.7)
% removal by pH adjust to 7.5 - 8.0		85	96	15	13	89	71 (0)
% removal after pH adjust and ferrate dose given	0	0	0	0	0	0	0
	1.5						(76)
	10	7*	14	20	11	64	72
	20	13	29	35	24	73	76
	40	20	43	60	47	86	90
	100	47	71	82	79	91	93

* Percent removal calculation after pH adjustment.

** Bracketed entries are for lime pretreated wastewater.

(1), (2), (3) are sample numbers as mentioned in the text.

produces a relatively stable sol of iron hydroxide that requires post filtration to achieve high trace metal removal. Ferric coagulation of trace metals does not have this liability.

Economic considerations for electrolytic generation of ferrate from scrap iron at a steel plant suggest that production may be on the same order as the related oxidant, permanganate (1).

CONCLUSIONS

Based on the work described herein several conclusions are:

1. Ferrate has promise for solids and metal removal in steel plant wastewaters.
2. Lime pretreatment is effective to reduce ferrate doses but post filtration may be required
3. Complex dependence on solution chemistry is observed for lime plus ferrate or ferrate only treatment.
4. Comparison of ferrate and ferric show varying optima dependency on the metal ion to be removed. Cadmium is better removed by ferrate at low pH and lead by ferric.
5. Theoretical equilibrium computations show considerable difference from experiment except for Pb removal.
6. Removal of metals in actual wastewaters were high at low dose when provision for adequate solid-liquid separation is included.
7. Conjunctive oxidation benefits of ferrate should be explored for priority pollutant removal in steel plant wastewaters.

ACKNOWLEDGEMENT

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PILOT EVALUATION OF ALKALINE CHLORINATION ALTERNATIVES FOR BLAST FURNACE BLOWDOWN TREATMENT

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INTRODUCTION

Ammonia and cyanide are among the pollutants found in blast furnace blowdown for which Best Available Technology Economically Achievable (BAT) effluent limitations have been proposed. In order to meet these limitations, both ammonia and cyanide may have to be removed prior to discharge. Alkaline chlorination is a potential process for achieving removal of both pollutants from a single wastewater source. In keeping with the goals of BAT, alternative treatment systems incorporating alkaline chlorination have been evaluated with respect to performance and cost-effectiveness in removing ammonia and cyanide from blast furnace blowdown. The three alternative treatment systems were single-stage alkaline chlorination, two-stage alkaline chlorination and combined air stripping/alkaline chlorination. Pilot plant testing was conducted to develop performance data, operability and cost estimates for full scale blowdown treatment incorporating alkaline chlorination.

PROCESS ALTERNATIVES

The three alternative alkaline chlorination treatment systems were tested to determine their effectiveness for the removal of both ammonia and cyanide. The unit processes that constituted the treatment systems included breakpoint chlorination and air stripping for ammonia removal, alkaline chlorination for oxidation of cyanide, dechlorination for reduction of residual chlorine, and flocculation, clarification and filtration for removal of the suspended solids generated by these chemical treatment processes.

AMMONIA REMOVAL

Ammonia removal from blast furnace blowdown can be accomplished by either breakpoint chlorination or air stripping. Theoretically, complete ammonia removal can be achieved by either method. In breakpoint chlorination, the degree of ammonia removal by chlorination is a function of pH and chlorine dosage (1). As chlorine is added to the wastewater, the combined chlorine residual increases, indicating the formation of chloramines. An increasing dosage of chlorine results in a decrease of combined residual to a minimum or breakpoint. Further chlorine addition results in a free chlorine residual signifying complete ammonia oxidation. Ammonia is oxidized to nitrogen gas by the following reaction:

$$2\ NH_3 + Cl_2 \rightarrow N_2 + 6\ HCl$$

The optimum pH range for breakpoint chlorination is 6.5 to 8.5. Outside of this range the chlorine dosage required to reach breakpoint increases and the reaction rate decreases. If insufficient chlorine is present to achieve breakpoint chlorination, chloramines will remain. Under alkaline conditions monochloramine predominates.

In air stripping, ammonium ions are converted to the dissolved gaseous phase by raising the pH (2). The wastewater is then introduced into a stripping tower where air flow is induced in a counter-current mode to liberate the ammonia gas. The rate of ammonia removal is a function of pH and temperature. As the pH is raised from neutral pH, ammonium ions are converted to the ammonia (NH_3) form as shown by this equation:

$$NH_4^+ \rightarrow NH_3 \text{ (gas)} + H^+$$

At pH 12 only the dissolved ammonia gas is present. Normally, the optimal pH for air stripping is between 10.5 and 11.5, a level that insures that the ammonia is in the dissolved gaseous phase. Greater ammonia removal is obtained at higher temperatures. In the case of a blast furnace recycle system, the temperature year round would be favorable.

Once the ammonia is in the gaseous phase, there are two factors which affect the transfer from liquid to gas:

1. Mass transfer
2. Ammonia equilibrium

The resistance to mass transfer between liquid and air is at a minimum when water droplets are being formed and reformed. Normally this formation and reformation of water droplets is most effectively accomplished in a packed tower as opposed to a tower without packing (cooling tower). The approach to ammonia equilibrium in the air around a water droplet will affect the transfer. Therefore, air flow is usually induced to purge the ammonia. As the air to liquid ratio increases, the ammonia transfer increases. The potential of employing air stripping as a preliminary step to the alkaline chlorination process was incorporated in the pilot plant as an alternative to remove ammonia, thus reducing the chlorine demand.

CYANIDE REMOVAL

Alkaline chlorination for cyanide removal is achieved by raising the pH of the wastewater and dosing with chlorine. In an alkaline system (pH > 8.5), cyanide is oxidized to cyanate according to the following reaction:

$$NaCN + 2\ NaOH + Cl_2 \rightarrow NaCNO + NaCl + H_2O$$

The reaction rate increases with pH. At pH 10 to 11, the reaction time is approximately 5 to 7 minutes.

Cyanate undergoes further oxidation with excess alkali in the presence of free chlorine according to the following reaction:

$$2NaCNO + 4\ NaOH + 3Cl_2 \rightarrow 2\ CO_2 + 6\ NaCl + N_2 + 2\ H_2O$$

This reaction proceeds rapidly at pH 8.5 to 9.0, requiring 10 to 15 minutes for completion. However, at pH 10 the reaction is slow and only partial cyanate destruction may be achieved in a practicable detention time.

The complete destruction of cyanide to carbon dioxide and nitrogen theoretically requires 6.82 parts of chlorine per part of free cyanide and 1.225 parts of hydrated lime per part of chlorine applied (3). In practice it requires more chlorine to oxidize other chlorine demanding compounds. Lime requirements will vary depending on the initial alkalinity of the wastewater.

Alkaline chlorination of cyanide wastes has been successfully applied in the metal plating industry where high cyanide concentrations (dumped plating baths) of 500 to 1,500 ppm are not uncommon (3,4,5). The usual treatment scheme employs a two-stage reactor system. The first stage is maintained at a pH of 10 to 11, optimum for oxidation of cyanide to cyanate. In the second stage reactor, the pH is controlled at approximately 8.5 for optimum cyanate oxidation. Chlorine may be added in both stages by independent control systems to insure an adequate supply.

DECHLORINATION

Following alkaline chlorination, dechlorination must be employed to remove residual chlorine prior to discharge. Dechlorination may be accomplished by addition of sulfur dioxide, sodium sulfite, sodium bisulfite or sodium metabisulfite (1). Addition of any of these compounds provides a source of bisulfite (HSO_3^-) either directly or by hydrolysis. The bisulfite reduces hypochlorite to hydrochloric acid according to the following reaction:

$$HOCl + HSO_3^- \rightarrow Cl^- + SO_4^= + 2H^+$$

This reaction is virtually instantaneous and, thus, complete reduction of hypochlorite is simply a function of adequate mixing. If chloramines are present from incomplete oxidation of ammonia, they will be reduced to ammonia and hydrochloric acid according to the following reaction:

$$NH_2Cl + HSO_3^- + H_2O \rightarrow Cl^- + SO_4^= + NH_4^+ + H^+$$

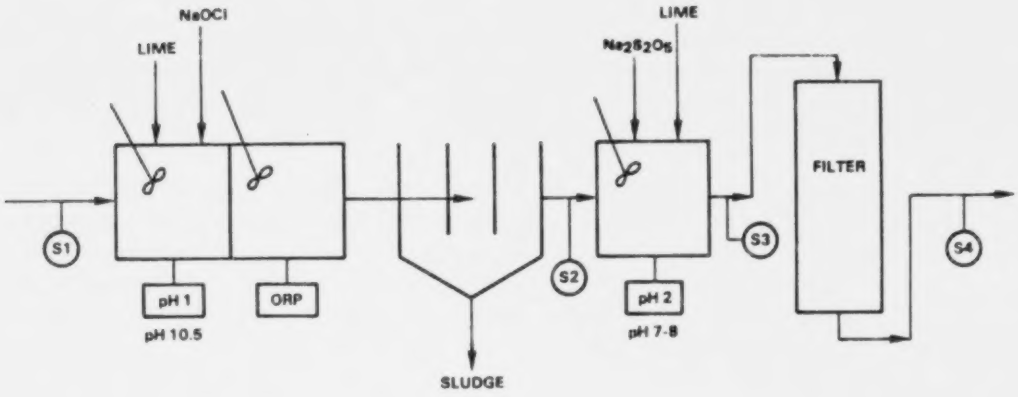
This reaction is also instantaneous. Thus, any ammonia that was converted to chloramines upon chlorination will not be removed from the wastewater.

Dechlorination reduces alkalinity by releasing protons. Destruction of high chlorine residuals results in a depression of pH. The degree of pH depression depends upon the alkalinity of the wastewater. Neutralization may be required to adjust the pH to a suitable level for discharge.

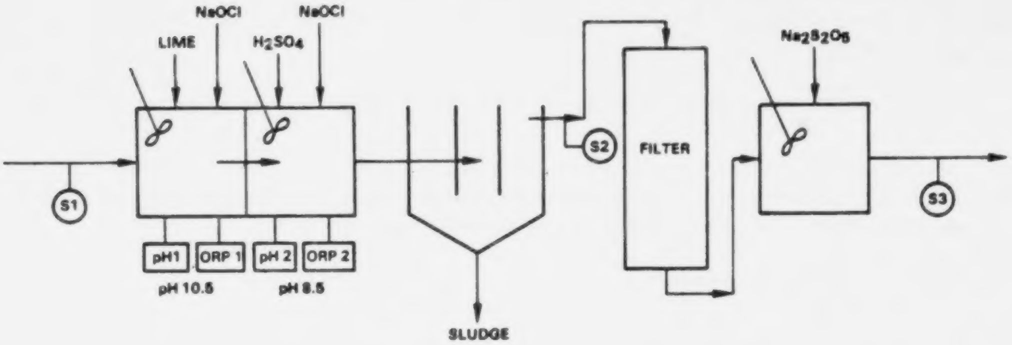
INTEGRATED TREATMENT

The unit processes previously discussed were combined to provide three different integrated processes to be demonstrated for achieving effective removal of ammonia and cyanide. The process flow trains that were demonstrated were single-stage alkaline chlorination, two-stage alkaline chlorination and air stripping followed by two-stage alkaline chlorination, as shown in Figure 1. Variations of the two-stage process aimed at cost reduction were piloted. The objective was to determine whether these variations could effectively be operated and still achieve both cyanide and ammonia oxidation.

1. SINGLE-STAGE ALKALINE CHLORINATION


NaOCl
LIME
LIME
$Na_2S_2O_5$
FILTER
S1
S2
S3
S4
pH 1
ORP
pH 2
pH 10.5
pH 7-8
SLUDGE

2. TWO-STAGE ALKALINE CHLORINATION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NaOCl
LIME
H_2SO_4
$Na_2S_2O_5$
FILTER
S1
S2
S3
pH1
ORP 1
pH 2
ORP 2
pH 10.5
pH 8.5
SLUDGE

3. COMBINED AIR STRIPPING/ALKALINE CHLORINATION

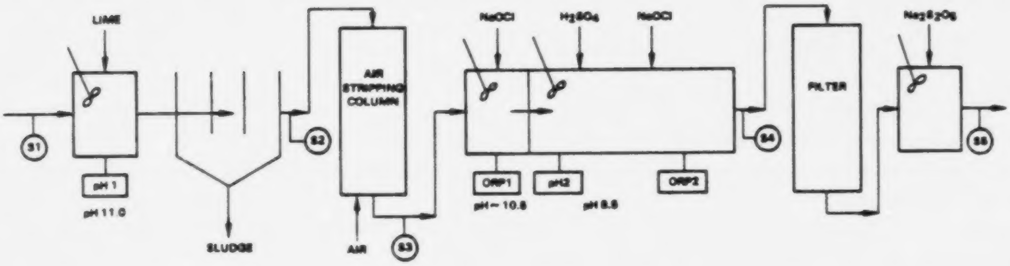
LIME
AIR STRIPPING COLUMN
NaOCl
H_2SO_4
NaOCl
FILTER
$Na_2S_2O_5$
S1
S2
S3
S4
S5
pH 1
pH 11.0
SLUDGE
AIR
ORP1
pH2
ORP2
pH ~ 10.5
pH 8.5

Figure 1. Alternative Process Flow Trains

The two-stage process would normally be employed to achieve both cyanide and ammonia removal by alkaline chlorination. This system, similar to that used for cyanide plating wastes, is sized to allow sufficient detention time for all cyanide to be oxidized to cyanate in the first reactor. The second reactor is sized to allow sufficient detention time for all cyanates and ammonia to undergo complete oxidation. The reactor effluent is then clarified, filtered and dechlorinated prior to discharge.

Single-stage alkaline chlorination varies from the normal two-stage alkaline chlorination process in that the pH is maintained at 10 to 11 in a single reactor and not readjusted throughout the treatment system until discharge. This system would be sized to allow sufficient time for oxidation of all cyanide to cyanate and for partial oxidation of cyanate and ammonia in one reactor. The detention time in the flocculator and clarifier is utilized to provide sufficient time for oxidation of cyanate and ammonia, since pH 10 to 11 is not favorable for this reaction to occur in a practicable reactor detention time. Prior to discharge, the effluent is dechlorinated and may be filtered for polishing.

The combined air stripping and alkaline chlorination alternative reduces the chlorine requirements by air stripping the ammonia while providing favorable conditions for the complete oxidation of cyanide. The optimum pH level of 10.5 to 11.5 is maintained through the air stripping tower to provide ammonia removal. The alkaline chlorination step is sized to allow sufficient time for the cyanide to be oxidized to cyanate at pH 10.5 to 11.5 in the first reactor. The second stage reactor is sized to provide adequate detention time for the cyanates to be oxidized and as a polishing step to oxidize ammonia not removed by air stripping. Filtration is employed to remove residual solids. Following filtration the waste is dechlorinated before discharging the treated blast furnace blowdown.

TESTING PROGRAM DESCRIPTION

A trailer-mounted physical/chemical treatment pilot plant with facilities for chemical feed, flocculation, clarification, and filtration was employed to demonstrate the alternatives for alkaline chlorination treatment process. The configuration of the pilot equipment is illustrated in Figure 1.

The mobile pilot plant was operated to demonstrate alkaline chlorination of blast furnace blowdown at two different steel mills. The source of water at both sites was the blowdown from blast furnace gas scrubbing recycle system. Prior to blowing down, the recycled water had undergone clarification for suspended solids removal and cooling for thermal reduction.

Bench scale tests were performed at the outset of each pilot study to determine the oxidation-reduction potential (ORP) set points and estimate chemical requirements. Jar tests of varying chlorine dosages were conducted to simulate pilot plant operating conditions. The pH was adjusted to operating levels using lime and sulfuric acid as necessary. During these tests ammonia, cyanide, pH, ORP, and total and free residual chlorine were monitored. These parameters were then defined as functions of chlorine dosage. The chlorination breakpoint and oxidation potential levels could then be determined.

The importance of the bench tests should not be overlooked because of the influence of water quality on the treatment process. Chlorine demand and ORP set points vary among wastewaters. ORP is very pH-dependent and therefore tight pH control must be maintained. Timing is important to allow for time-dependent reactions such as cyanate oxidation to reach completion, and can affect monitoring of both ORP and residual chlorine.

The pilot plant was operated at 6 gallons per minute (gpm) through the rapid mixing tank for chemical treatment and clarifier for suspended solids removal. A flow rate of 5 gpm was maintained through the dual media filtration system for polishing. At these flow rates the detention time was 8.3 minutes in the flocculator and 2 hours in the clarifier. The clarifier overflow rate was 350 gallons per day per square foot (gpd/ft^2) or 0.25 gpm/ft^2. The filter loading rate was 5 gpm/ft^2. The sludge accumulated in the bottom of the clarifier was wasted at the rate of production.

All pumps and rapid mixers were controlled from a control panel. There were two pH meters and two ORP meters located at this panel. Both pH and ORP were indicated and recorded. Associated with these meters were controllers which were employed to regulate chemical feed based on specified set points and in response to pH and ORP probes.

SINGLE-STAGE ALKALINE CHLORINATION

Wastewater was introduced into the first reactor with a 10-minute detention time where a slurry of hydrated lime was applied to maintain pH 10.5. The lime addition was controlled by a pH controller with its input probe located in the first reactor. Sodium hypochlorite was also applied in the first reactor. An ORP controller was employed for sodium hypochlorite addition. The ORP setpoint (+700 mV) was determined in the bench test as the level at which free chlorine residual existed. The input probe was located in a second reactor with a detention time of 10 minutes to allow additional reaction time before measuring the potential level. No chemicals were added to the second reactor. The flocculator-clarifier detention time provided additional reaction time for cyanate and ammonia oxidation (providing free chlorine is still available).

Overflow from the clarifier was dechlorinated by the continuous addition of sodium metabisulfite. The metering rate and strength was determined by analysis of grab samples for free and total chlorine residual. Dechlorination resulted in a large drop in pH which was adjusted by addition of a lime slurry, as controlled by a pH controller. Neutralized wastewater was pumped from dechlorination tank to the dual media filter for polishing prior to discharge.

TWO-STAGE ALKALINE CHLORINATION

Blowdown was introduced in the first stage reactor with a 10-minute detention time. A slurry of hydrated lime controlled by a pH controller with its input probe located in this reactor was applied to maintain pH 10.5. Sodium hypochlorite was also added in the first reactor. Hypochlorite addition was controlled by an ORP controller with its probe located in the first stage reactor. The ORP set point was determined in the bench test to be +280 mV. The wastewater then passed by gravity into the second stage reactor. Sulfuric acid was applied to lower the pH to 8.5, as controlled by pH controller with its probe located in this reactor. Sodium hypochlorite addition in this reactor was controlled by a second ORP controller with its probe located in the reactor. The set point was +780 mV as determined in a bench test. Based on the free chlorine remaining, the ORP set point was fine tuned to maintain a minimum free chlorine residual. The flocculator-clarifier provided additional detention time for cyanate oxidation.

Overflow from the clarifier was pumped through the filter for additional polishing and then dechlorinated. Dechlorination was accomplished by the continuous addition of metabisulfite. By optimizing the control of the ORP set point in both reactors, a very low free chlorine residual could be maintained, therefore minimizing the chemical requirement for dechlorination.

COMBINED AIR STRIPPING/ALKALINE CHLORINATION

Wastewater was introduced to a reactor with a 10-minute detention time. Here a slurry of hydrated lime was applied to maintain pH 11 by use of a pH controller. Effluent from the reactor passed into the flocculator-clarifier for flocculation and solids separation. Overflow from the clarifier was pumped to the air stripping column. The packed stripping column was operated in a counter-current flow mode with introduction of wastewater at the top and air at the bottom.

In the combined treatment system, the wastewater from the column was pumped into the first stage reactor with a 10-minute detention time. Sodium hypochlorite addition to this tank was controlled by an ORP controller. The ORP set point (+300 mV) was determined by a bench test conducted on the air stripping column effluent. The wastewater passed by gravity into the second stage reactor with a detention time of 60 minutes. Sulfuric acid was applied to maintain the pH to 8.5, as controlled by a pH controller. Additional sodium hypochlorite was introduced into the second stage reactor based on a second ORP controller with the probe located in the reactor. The ORP set point (+850 to +900 mV) was set based on the bench test and fine tuned daily to maintain a minimum chlorine residual.

The overflow from this reactor was pumped through the dual media filter for polishing and was then dechlorinated with metabisulfite. The metering rate and strength was determined by monitoring the chlorine residuals. By optimizing the ORP setting to maintain a low chlorine residual, the amount of metabisulfite required could be kept to a minimum.

SAMPLE COLLECTION AND ANALYSIS

During the operation of each integrated treatment process train, composite samples were collected for a twelve hour test run. Normally the pilot plant influent and effluent was collected and analyzed for each run. For each process train, other selected sampling points, such as clarifier and stripping column effluent, were collected and analyzed. Grab sampling across the process trains (including the reactors) was conducted daily to monitor the process for ammonia, cyanide, cyanates and other parameters. Additional grab samples were also taken daily for pH, temperature, turbidity and chlorine residual as a means of providing on-site control.

All samples were divided, preserved and analyzed according to EPA Methods (6) and Standard Methods (7) at the end of each compositing period. When samples were to be collected and analyzed for priority pollutant organics, additional sample division was required. Sample containers were properly prepared in glass bottles supplied solely for priority pollutant organics.

RESULTS AND DISCUSSION

Of the pollutant parameters that were monitored, ammonia and cyanide were the key parameters by which alkaline chlorination was evaluated. These results have been summarized for each process alternative in Tables 1 and 2. Also important were the presence and fate of organic priority pollutants in the system, particularly trihalomethanes (THM) which were formed during chlorination. These results have been summarized in Table 3 for each process alternative. In examining these results, it is important to bear in mind that the single-stage process alternative and the other two process alternatives were demonstrated at different blast furnace recycle systems. Valid comparisons may be made based on trends, achievable effluent concentrations, process operability and relative estimated costs. Comparisons between absolute effluent concentrations cannot be made because blowdown water characteristics were different for different recycle systems and even within a given recycle system. Water quality in these systems is a function of several variables including blast furnace burden, degree of recycle, quench water quality and the influence of extraneous water sources which are unrelated to the blast furnace system.

AMMONIA REMOVAL

Effective removal of ammonia was achieved by all three process alternatives. The two-stage and combined air stripping process alternatives yielded more consistent effluent levels than the single-stage alternative. This may be attributed to the tighter process control of two-stage operation over single-stage operation. The operating pH of the second stage was more favorable for ammonia and cyanate oxidation. It is equally important that cyanates be oxidized as well as ammonia because of their tendency to hydrolize to ammonia. For the single-stage process, higher effluent ammonia concentrations corresponded to presence of cyanates in the effluent.

TABLE 1. COMPARISON OF AMMONIA AND CYANIDE DATA

BY ALKALINE CHLORINATION ALTERNATIVE	INFLUENT (ppm) MEAN	INFLUENT (ppm) RANGE	EFFLUENT (ppm) MEAN	EFFLUENT (ppm) RANGE
SINGLE-STAGE				
AMMONIA	115	43-180	4.1	1-23
CYANIDE	5.6	0.01-28	0.02	0.01-0.19
TWO-STAGE				
AMMONIA	72	65-97	1.2	0.1-4.2
CYANIDE	4.2	1.5-75.	0.25	0.01-1.4
COMBINED AIR STRIPPING				
AMMONIA	38	31-61	4.0	0.1-8.5
CYANIDE	13	3.2-23	8.0	1.2-24

TABLE 2. AMMONIA DATA SUMMARY: COMBINED AIR STRIPPING/ALKALINE CHLORINATION

		STRIPPING COLUMN		ALKALINE CHLORINATION		TOTAL SYSTEM
	INFLUENT	STRIPPING EFFLUENT	PERCENT REMOVAL	FINAL EFFLUENT	PERCENT REMOVAL	PERCENT REMOVAL
COMPOSITE SAMPLES						
MEAN	38 ppm	15 ppm	60%	4.0 ppm	79%	91%
MINIMUM	31	9.2	49	0.1	68	86
MAXIMUM	61	20	66	8.5	99	>99
GRAB SAMPLES						
MEAN	43	16	63%	3.1	80%	91%
MINIMUM	28	11	53	<0.1	63	77
MAXIMUM	62	20	72	7.4	>99	>99

TABLE 3. COMPARISON OF TRIHALOMETHANE DATA

TRIHALOMETHANE BY ALKALINE CHLORINATION ALTERNATIVE	INFLUENT (ppb)	EFFLUENT (ppb) MEAN	RANGE
SINGLE-STAGE			
CHLOROFORM	ND	750	530-1,000
BROMOFORM	ND	1,700	1,000-2,800
DICHLOROBROMOMETHANE	ND	1,290	1,000-1,600
CHLORODIBROMOMETHANE	ND	2,600	2,500-2,700
TWO-STAGE			
CHLOROFORM	ND	28	11-40
BROMOFORM	ND	890	830-990
DICHLOROBROMOMETHANE	ND	52	22-88
CHLORODIBROMOMETHANE	ND	117	110-130
COMBINED AIR STRIPPING			
CHLOROFORM	ND	<10	<10
BROMOFORM	ND	190	160-200
DICHLOROBROMOMETHANE	ND	10	<10-10
CHLORODIBROMOMETHANE	ND	45	41-49

ND - NOT DETECTED

The presence of cyanates indicated that chlorine addition was probably insufficient since cyanates had not been oxidized. By including a point of chlorine addition in the second stage as well as in the first stage. the two-stage system was better able to meet the chlorine demand for ammonia and cyanate oxidation. Maintaining sufficient chlorine throughout the chlorination reaction portion of the system by trimming the dosage to the demand was the key to maximizing completion of the oxidation reactions.

From the combined air stripping/alkaline chlorination results (Table 2). it is evident that about 60 percent of the influent ammonia was removed across the air stripping step. and about 80 percent of the remaining ammonia was removed by the alkaline chlorination step. During this testing phase. ammonia removal by air stripping was limited by the pilot plant equipment rather than by the stripping process itself. The preliminary air stripping testing. which defined ammonia removal efficiency as a function of the air to liquid ratio. demonstrated that 75 percent ammonia removal was approaching the practical limit for stripping of this particular wastewater with the equipment that was employed (Figure 2). This corresponded to an air to liquid ratio of 2,000 to 2,200 (volume basis). At these air to liquid ratios and greater. very little gain in removal was achieved for large increases in air flow. Maximum practicable ammonia removal would be achieved at air to liquid ratios from 1,500 to 2,000. However. within the limits of available blower capacity. these air to liquid ratios would require a process water flow that was too low for adequate pilot plant operation of alkaline chlorination. Therefore. actual operating air to liquid ratios were 1,000 to 1,400.

The removal of the ammonia remaining in the air-stripped wastewater by the alkaline chlorination step resulted in fairly consistent effluent levels. However. the mean effluent concentration was somewhat higher than was expected based on the performance of the two-stage alkaline chlorination testing conducted

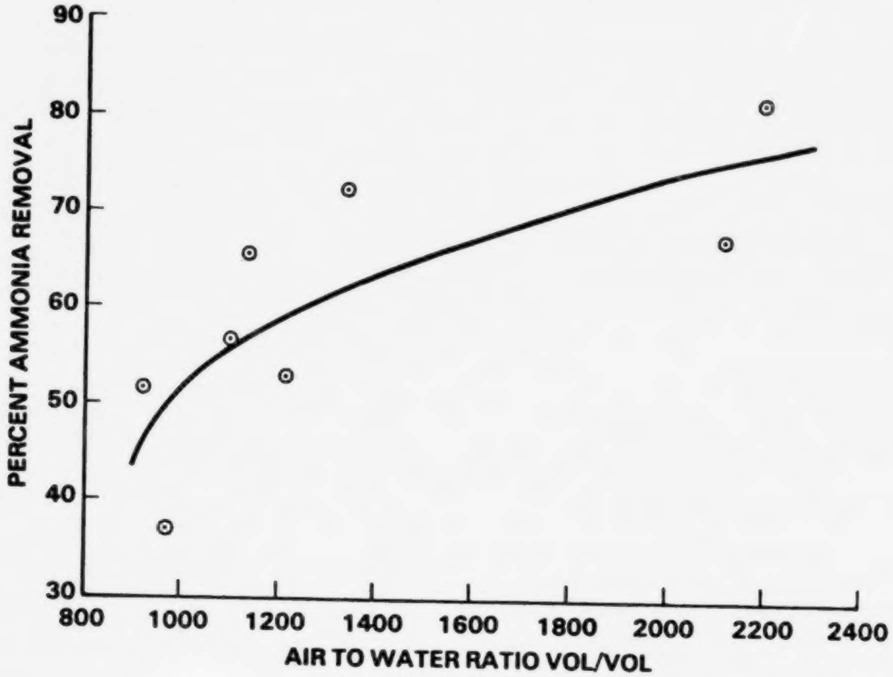

Figure 2. Ammonia Removal as a Function of the Air to Water Ratio

at the same wastewater source under similar operating conditions and with a similar degree of process control. It appeared that during the combined air stripping/alkaline chlorination testing phase, the blowdown water quality changes may have affected operation and tested the limits of two-stage process control. Removal of ammonia was consistent for the total system. However, there was some variation in the quantity of ammonia stripped from the system. Regardless of the ammonia remaining after stripping, it was removed by the alkaline chlorination step, resulting in the consistent net removal of ammonia across the entire treatment system. Such behavior suggested that the alkaline chlorination step was achieving oxidation of ammonia essentially to the maximum possible extent.

The resulting higher effluent ammonia concentrations may be attributed to the presence of cyanate in the effluent. The observed trend was that effluent ammonia concentrations were generally higher when the effluent cyanate concentrations were higher, indicating that some of the cyanate had probably hydroized to ammonia. Effluent cyanate concentrations ranged from 2.0 to 20 ppm. Another generally observed trend was that effluent cyanate concentrations decreased with an increasing free chlorine residual maintained in the second stage reactor. The highest effluent cyanate concentrations were observed for the lowest free chlorine residuals, particularly for those less than around 5 ppm.

The presence of both cyanates and low free chlorine residuals indicated that the chlorine demand for complete cyanate oxidation fell short of being met as a result of a change in influent water quality. This change was evident in the data presented in Table 2 and was an apparent result of a blast furnace that was rapidly approaching the end of its campaign. The effect of a different influent water quality may have, in fact, demonstrated the response of the alkaline chlorination process to water quality changes within a given recycle system.

CYANIDE REMOVAL

Effective removal of cyanide was achieved by both the single-stage and two-stage processes, whereas the combined air stripping process achieved only partial cyanide removal. Effluent total cyanide concentrations were consistently low for the single-stage process, very often below the detectable limit. For the two-stage process, effluent total cyanide concentrations were higher with greater fluctuations from the mean. This may be attributed to differences in the characteristics between the different wastewater sources. The wastewater from the system where the two-stage and combined air stripping processes were demonstrated was found to have complex cyanides, such as ferrocyanides, occasionally present. This transient presence of ferrocyanides would explain the wide range of effluent total cyanide values. Complex cyanides are not amenable to chlorination, and therefore would not be oxidized by the process.

For the combined air stripping process, influent cyanide concentrations increased considerably over what they had been during the two-stage process testing phase. These increases were an apparent result of a blast furnace approaching the end of its campaign. Associated with the increase in total cyanide was an apparent increase in complex cyanides, particularly ferrocyanides witnessed by the characteristic blue coloration in the wastewater. The presence of complex cyanides would account for the high total cyanide concentrations in the effluent.

TRIHALOMETHANE FORMATION

While alkaline chlorination was effective in removing ammonia and cyanide, it was equally effective in producing THM's, which may be creating a potentially worse problem environmentally. No THM's were detected in the untreated blowdown, yet they were found in relatively high concentrations after chlorination. The concentrations of THM's formed were different for all three process alternatives. Differences between the single-stage process and both the two-stage and combined air stripping processes may be attributed to the different sources of blowdown. In all probability, these differences in concentrations were due to the quantity and type of THM precursors present in each of the wastewaters.

The differences in effluent THM concentrations between the two-stage and combined air stripping processes may be attributed to reduced influent concentrations of THM precursors during the combined testing phase. The reduced precursor concentrations were probably a result of the observed changes in blowdown water quality previously mentioned and may also have been a result of removal by air stripping. In the absence of specific precursor data, comparisons of possible precursor trends may be made with respect to ammonia as an indicator of recycle system water quality. For the particular recycle system under consideration, ammonia had been found to be a fairly consistent indicator of the cycles of concentration. From the time the two-stage process testing was conducted to the time of that of the combined air stripping process, blowdown ammonia concentrations decreased by 47 percent on the average while THM concentrations decreased by 60 to 80 percent, on the average. This suggested that THM precursor concentrations may have decreased by means other than by dilution from additional make-up water (the principal reason for decreased ammonia concentrations). Removal of precursors by air stripping may have occurred, reducing THM formation.

While the effluent THM concentrations were different for all three process alternatives, the trend was clear: one of the side effects of alkaline chlorination was the formation of toxic THM's. It should be noted that the drinking water standard for total THM's (the sum of the four THM's shown in Table 3) is 100 ppb (8). While drinking water standards do not provide a valid comparison, it would suffice to point out that the total THM's produced during alkaline chlorination and present in the final effluent exceeded the drinking water standard by 2.5 to 70 times.

PROCESS CONTROL

The pilot plant employed in this evaluation was sized to treat a nominal flow of 6 gpm. This size unit provided an opportunity to develop data on the performance of a larger full scale unit. However, there are many inherent problems in controlling small physical/chemical processes such as these three alkaline chlorination treatment processes.

A unit this size is difficult to control due to the on/off nature of many of the chemical feed controls and the strong concentrations or form of chemicals which had to be employed in order to maintain a sufficient supply for a 12-hour unattended test run. The chemical control system on a larger treatment stream would be trimmed to provide more consistent control by employing integrated and/or proportional controllers and by applying chemicals in forms that would insure improved metering and mixing. For example, the use of chlorine gas and sulfur dioxide in place of sodium hypochlorite and sodium metabisulfite provides these benefits as well as a chemical cost savings. Another example is the introduction of lime to the mixing tank which was based on the signal from an on/off pH controller that actuated a solenoid valve. The concentrated lime slurry of 8 to 12 percent by weight had to be utilized in order to provide a 12-hour supply. This sometimes resulted in erratic pH control. These two problems, the on/off controls and form and concentration of chemicals, were inherent problems to all alternatives that were piloted. Setting this aside, unique process control limitations were also encountered for each individual integrated treatment system.

In the single stage system, the addition of chlorine is a potential problem. To date the only satisfactory monitoring/control technique for continuous cyanide treatment by alkaline chlorination is the actual potential levels of the oxidation reactions. These potential levels (plateaus) are dependent on the wastewater and must be empirically determined. That corresponding to the raw waste is called the reduced potential level. The cyanate potential level is the potential level after just sufficient chlorine has been added to completely convert all cyanide to cyanates. In the presence of ammonia, further chlorine addition results in the formation of chloramines. The cyanate and chloramine potential levels are identical. The potential level of the wastewater will remain at this plateau unless sufficient chlorine is added to oxidize all the ammonia and cyanates. At this point, further chlorine addition results in a free chlorine residual raising the potential level to a final plateau signifying complete oxidation.

The single-stage chlorination does not provide optimum pH conditions for either ammonia or cyanate oxidation. Optimum oxidation of both ammonia and cyanate occurs at approximately pH 8.0 to 9.0. Ammonia oxidation produces acid which may lower wastewater pH somewhat (depending on alkalinity and the amount of ammonia reacted) as oxidation occurs after the wastewater leaves the pH controlled (10.5) reactor. However, this pH depression will probably not be sufficient to lower the pH to a favorable range.

The additional detention time provided in the clarifier may not be effectively utilized for cyanate oxidation if the wastewater pH remains high or free chlorine is not available. The rate of cyanate oxidation by free chlorine ranges from approximately 10 minutes at pH 8.0 to about 35 minutes at pH 9.5. Control difficulties result if sufficient retention time is not allowed for completion of the reaction. Chloramines, formed by chlorine addition after cyanate formation, will not destroy cyanates. Therefore sufficient chlorine must be added to react with all ammonia and cyanates before the free chlorine potential level can be reached and maintained. If insufficient chlorine is added, the free chlorine potential level may be momentarily reached as all ammonia is reacted. However, the potential level will fall back to the cyanate level as the relatively slow cyanate oxidation exhausts the available free chlorine, making chlorine addition very difficult to control (3).

In the two stage alkaline chlorination flow train, the addition of chlorine was controlled in a manner favorable for ammonia and cyanate oxidation. The first reactor pH of 10.5 and ORP control at +280 mV was set to maintain the pH and ORP levels for complete conversion of all cyanide to cyanate.

In the second stage reactor, the pH was maintained at 8.5, and chlorine addition was controlled to the ORP set point of +780 mV (the second oxidation potential level), providing favorable conditions for the oxidation of ammonia and cyanate. At this pH the ammonia is oxidized almost immediately in the presence of sufficient chlorine. The ORP reading in this reactor will not be a false reading as this potential level can be maintained within this reactor, whereas in the single stage system this potential level cannot be guaranteed throughout the flow train. Control of chlorine addition in this system was fine tuned to operate so that excessive chlorine was not introduced into the reactors as occurred in the single-stage alkaline chlorination system while still providing consistent removal of ammonia and cyanide.

In the combined air stripping/alkaline chlorination process, control was similar to the two stage operation. The main difference is that much of the ammonia removal was achieved prior to the alkaline chlorination process. Fine tuning of the alkaline chlorination step appeared to be easier with less ammonia present.

COST COMPARISON

Construction and operating costs were estimated for the three treatment alternatives. Construction costs were developed for treatment facilities sized to handle the blowdown rate of 300 gpm. This represents the EPA model plant production of 6,000 tons/day and maximum blowdown rate of 70 gal/ton as presented by the EPA for the Iron Making Subcategory (9). Operating costs include chemical, labor, power, and maintenance costs. Chemical usage was estimated based on results of the pilot plant operation and bench scale data. No scale-up factors were used since they were considered unnecessary for this physical/chemical treatment. The BAT model employed to develop costs was designed as an "add on" facility to an existing BPT system and therefore assumes the effluent is of BPT quality. However, the chemical costs will be site-specific based on concentrations of ammonia, cyanide, cyanates, thiocyanates, iron, and sulfide in the blowdown. Therefore, the chemical cost which represented 60 to 70 percent of the annual operating cost could be significantly higher or lower.

The amortized capital costs and the annual operating costs were summarized in Table 4 to establish total annual costs for each alternative. These costs ranged from a minimum of $518,000 for combined air stripping/alkaline chlorination to a maximum of $571,000 for the two-stage alkaline chlorination. It should be noted that the major cost differences are due to the additional equipment required. Additional tanks, mixers, and control systems are required to convert the single stage to two stage alkaline chlorination. The additional capital cost for the combined air stripping/alkaline chlorination over the two stage alkaline chlorination represents additional tankage, pumps, and an air stripping tower with fans. However, the 20 to 25 percent reduction in annual operating cost for the combined air stripping/two stage alkaline chlorination is the result of reducing the chlorine requirements. It should be noted that the reduced chemical requirement for combined treatment is slightly offset by additional power usage. The total cost per 1,000 gal of influent has also been calculated for aid in comparing treatment alternatives. This cost, shown in Table 4, ranges from $3.45 to $3.72 per 1,000 gallons for the three treatment alternatives. The cost for treatment is very sensitive to chemical costs, which are very site-specific and represent approximately 25 to 40 percent of the total annual cost.

TABLE 4. COST COMPARISON

	SINGLE-STAGE ALKALINE CHLORINATION	TWO-STAGE ALKALINE CHLORINATION	AIR STRIPPING/ TWO STAGE ALKALINE CHLORINATION
TOTAL CAPITAL COST	**$1,202,000**	**$1,235,000**	**$1,333,000**
AMORTIZED CAPITAL COST(1)	**268,000**	**275,000**	**297,000**
ANNUAL OPERATING COST	**285,000**	**296,000**	**221,000**
TOTAL ANNUAL COST	**553,000**	**571,000**	**518,000**
TOTAL COST ($/1,000 GAL)	**$3.60**	**$3.72**	**$3.45**

1. AMORTIZED COST AT 18% FOR 10 YEARS.

SUMMARY

The degree of effectiveness in achieving oxidation of ammonia and cyanide by alkaline chlorination was limited by both process control and the water quality of the blowdown stream. For oxidation of ammonia, the differences in process performance among the alternatives were a result of both process control and water quality. Although absolute effluent ammonia concentrations could not be directly compared for the wastewaters treated, the degree of consistency in effluent levels reflected the degree of control achieved in each process alternative. In the two-stage and combined air stripping processes, a pH favorable for ammonia and cyanate oxidation was maintained in the second stage. Also tighter ORP control and chlorine addition were provided. In the single-stage process, oxidation of ammonia and cyanate was forced under unfavorable pH and, due to a single point of chlorine addition, a potentially inadequate supply of available chlorine.

The differences between effluent ammonia concentrations for the two-stage and combined air stripping processes appear to be a result of different water qualities within a given recycle system. This dependence on blowdown water quality indicated that, even for a given recycle system and even with tight process control, alkaline chlorination could not consistently achieve near zero effluent ammonia levels. However, removal of ammonia by air stripping substantially reduced chlorine requirements, allowing for more ease in operational control.

For the oxidation of cyanide, the differences in process performance among the alternatives were probably due to water quality, particularly with respect to the forms of cyanide present. The wastewater on which the single-stage process was piloted apparently contained no complex cyanides. Essentially complete destruction was demonstrated to consistently low effluent levels, demonstrating that alkaline chlorination readily oxidizes free cyanide. However, the wastewater on which the two-stage and combined air stripping processes were piloted was found to contain complex cyanides including ferrocyanide. Because the cyanide in ferrocyanide cannot be oxidized by chlorination, a range of effluent total cyanide levels resulted.

The formation of THM's by alkaline chlorination appear to be a function of the water quality, namely the presence and concentration of THM precursors in the blowdown stream. From the combined air stripping process testing, it appeared that some degree of precursor removal may have been achieved by the air stripping step. However, without more specific data on precursors, it is difficult to predict whether they are amenable to removal by air stripping and their fate in the alkaline chlorination process.

Estimated total annual costs were essentially the same for all three alternative treatment systems. Process modifications in the more conventional two-stage alkaline chlorination process did reduce costs a little, mostly by a reduction in chemical costs. The largest savings in chemical costs could be realized by the combined air stripping/alkaline chlorination process. This was somewhat offset by the increased capital cost for additional equipment, but not significantly less than either of the other two alternatives.

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CLOSING REMARKS

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Thank you for participating in this year's symposium. I would like for you to feel that this is your symposium, and that the role of the EPA Office of Research & Development is to serve as a catalyst by sponsoring the symposium and contributing to the call for papers. This year we had as many industry papers as papers from EPA ORD. We want a balanced and open forum. At future symposiums, it would be preferable to obtain an even greater industry participation. Many of this year's industry papers came in response to the call for papers, but many also were actively recruited or encouraged by either Bob McCrillis or myself. I'd like to ask you to please let us know if you are either conducting studies, or know of studies that you can recommend. Certainly contributions from other sources in addition to industry and government have made valuable contributions to these symposiums and are also actively sought.

I would like to acknowledge Frank Ayer who served as the symposium coordinator for this year's symposium as he has for the first two. Also, my colleague, Bob McCrillis, contributed much to this year's symposium by planning the air session. The session chairmen, Phil Masciantomio and Mike Hanson of U.S. Steel, Tom Barnes of Heckett, Bob Kaplan of Bureau of Mines, and Terry Oda of EPA did a fine job in encouraging meaningful discussions and the smooth operation of their sessions. Of course, the authors of these papers contributed most to the symposium. They, and the organizations they represent, deserve our appreciation for the efforts they made in preparing and presenting their papers.

The cooperative efforts and interest in environmental control demonstrated by the good participation in this symposium is encouraging. The next symposium is already being planned. Any suggestions you have to improve future symposiums would be appreciated.

UNPRESENTED PAPERS

APPLICATION OF SECOND GENERATION CHEMICAL SOLIDIFICATION/FIXATION PROCESSES TO IRON AND STEEL HAZARDOUS WASTE PROBLEMS

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ABSTRACT

The Iron and Steel Industries produce various waste sludges and other liquid, semi-liquid, and solid wastes which contain toxic metals and other hazardous constituents. Since 1970, several chemical solidification/fixation processes have been tested successfully for some of these waste streams but, primarily due to economics, have not been extensively used. The advent of RCRA has altered this situation and it is expected that solidification techniques will become important in the near future. In the meantime solidification/fixation technology has progressed from the few, early, broad-spectrum processes to engineered systems which can be most efficiently applied to specific waste streams. This paper will discuss the basic chemical systems in use today, the properties and limitations of these processes, and the delivery systems for applying them on a commercial basis. The design parameters which must be considered in choosing a solidification technology will also be described. In addition to process and system parameters, the interaction of the treated waste with the environment - in this case, the land disposal site - must be assessed. The paper will discuss final disposal practices as they affect, and are affected by, RCRA regulations and the test methods now used to establish whether a treated waste is hazardous. Current economics of various process types on typical waste streams will be compared with other alternatives for hazardous waste disposal.

INTRODUCTION AND DEFINITIONS

Ten years ago the words "chemical fixation" and "solidification were not part of the environmental engineer's vocabulary. By contrast, today we have several reputable and professional companies engaged specifically in the waste solidification business. However, in the minds of the prospective users of such processes, chemicals, equipment or services, there remains an aura of black magic which has not been completely dispelled. This is probably due primarily to the fact that until very recently most of the systems offered were considered proprietary and little information was available about the general chemical nature of the process.

Before going further, let us define the terms "chemical fixation", "stabilization", and "solidification". Recently ASTM Committee 34.09.01 approved the following definitions:

Solidification - The Treatment process by which a waste material is physically or chemically changed to create a solid which meets the criteria for its intended use. Examples: filtration, absorption, adsorption, admixing, encapsulation, etc.

Stabilization - A treatment process utilized to chemically modify a waste in order to render it suitable for its disposal or designated use. Such processes will include: ion exchange, oxidation-reduction, etc.

Fixation - A treatment process by which a waste material is rendered chemically and physically acceptable under applicable criteria for ultimate disposal, distribution, or use and will meet applicable federal and/or state standards for non-hazardous materials.

A SHORT HISTORY OF CHEMICAL SOLIDIFICATION AND FIXATION SYSTEMS:

With a few exceptions, the history of the development of these systems dates only from about 1970. Exceptions include the solidification of relatively small amounts of radioactive waste in drums, cemented backfill in certain mining operations, and the production of stabilized base courses for road construction using lime-flyash systems. There are also a number of isolated instances where waste residue generators - and especially waste disposal site operators - have used cement, lime, flyash, soil and various combinations of these materials to solidify liquid waste for disposal in non-secure landfills. Nearly all of the early work in commercial utilization of solidification processes was involved with a need for solidification only and rarely, if ever, were leaching tests or other technical evaluations of the performance of the processes conducted.

From the 1950's on the nuclear industry has recognized the need for solidification of radioactive waste in drums before these wastes could be shipped or buried at government controlled disposal sites in the United States. Much of the early liquid waste containing low level radioactivity was simply absorbed into various mineral absorbants such as vermiculite in drums, or solidified by making a concrete mixture with very large quantities of Portland cement. Sometime ago it was realized that the cement solidification system by itself had shortcomings. Large quantities of cement were required to assure that there would be no standing water in the drum after the cement cured. This resulted in a relatively large percentage of the drum volume being occupied by the cement instead of by the waste. Also the weight of the concrete so produced made the drums difficult to handle and increased the disposal cost. Since the major costs in the disposal of drummed radioactive wastes are in the cost of the drum, its transportation and its burial, the obvious was to reduce expense was to get more waste and less solidification agent into the drum. In addition, the drumming process with cement was not well controlled and was somewhat unpredictable, especially because of retarding agents which are present in many of the waste mixtures. Because of these problems, urea-formaldehyde and asphalt systems came into use to provide more consistency, lower weight and better space efficiency in the drum. By the late 1950's it was realized that the addition of sodium silicate to the Portland cement process usually provided better results overall than did the other processes.

For decades deep mines in Canada and elsewhere have been using Portland cement in combination with solid mine waste to produce cemented hydraulic backfill which helped eliminate the need for structural pillars or walls within an ore body. Portland cement was also used by various waste generators and operators of waste disposal sites but little documentation was ever made of these practices, probably because there was no evaluation of the characteristics of the solidified material.

Other than internal studies in various nuclear installations and at government nuclear regulatory agencies, there was no published work done on leachability, environmental degradation, or any other performance characteristics of solidified waste until IUCS and Chemfix, Inc. began applying scientific principles to fixation and solidification of various waste materials in the early 1970's. IUCS used a lime-flyash process which incorporated sulfates from the waste to contribute to strength development in the final solid. Chemfix used a patented process based on soluble silicates and silicate setting agents, primarily sodium silicate solution and Portland cement. Lime-flyash activities were aimed primarily at the sludges expected to be produced by lime/limestone scrubbing of flue gases to remove sulphur oxides. Operation of the lime-flyash process was designed to be at fixed installations where large quantities of waste were produced, or in areas such as construction sites where the solid produced could be used as a construction base for roads and parking lots. The cement-silicate process, on the other hand, aimed at a wider variety of sludges, especially those emanating from manufacturing, metal producing operations, and which contained large concentrations of the polyvalent metals which are considered toxic. Recognizing that most such wastes were stored in lagoons at the point of generation, this business was predicated on a mobile service whereby treatment units could be brought to the location, set up, and the waste removed and treated in a matter of days or weeks.

Beginning about 1975, chemical fixation and solidification systems began to receive attention from the government, from waste generators and from consulting engineering firms which had largely ignored this technology until that time. A series of projects were initated in the EPA's Office of Solid Waste Management to evaluate various solidification processes, to explore other possible systems and to develop the necessary testing and evaluation criteria. A number of organic solidification processes was announced as being in the development stage by both government funded and privately funded research organizations, and some hazardous waste management firms and engineering organizations began to tentatively offer solidification processes to their customers.

Chemical solidification and fixation systems have now become an accepted, if not widely understood, operation in the field of environmental control and waste disposal. New processes and variations of old ones are being announced with increasing frequency, and a rather bewildering array of processes, systems and chemicals has suddenly sprung on the market. These are partly listed and described in several recent articles and books, and have created a great deal of confusion because the promotional jargon suggests that there is a large number of totally different chemical systems involved. In fact, the number of systems which differ substantially from each other in the chemical sense is quite small, and will be described generically later in this paper. First, however, let us discuss the factors which should be considered in choosing a system.

SYSTEM DESIGN PARAMETERS

The solidification/fixation process is only one aspect of the overall system. The other factors include the waste itself, the waste source, the process engineering and operation parameters, the disposal site and the environmental impact of the system.

THE WASTE

Following are the primary characteristics of the waste which are considered in choosing a solidification system:

Toxicity

The toxicity (or potential toxicity) of the waste is of primary importance because it determines not only the process to be applied, but also the method of disposal. Toxic components of the waste can be described as either leachable or non-leachable with reference to the particular leaching test and leachant being applied. While most attention has been directed toward the leachable portion of the toxic components in the waste, the non-soluble components must also be given consideration because they represent a potential hazard if the actual leaching conditions in the environment are not the same as those tested in the laboratory, if the conditions change, or if there is a change in the disposal operation.

Perhaps the most common example of this problem is with metal hydroxide sludges. These sludges usually come from a water treatment plant where the pH of the system has been adjusted to achieve minimum solubility of the metals, precipitating them and allowing discharge of the clear water phase of the waste stream. Thus, the sludge as it is fed into the solidification system is essentially non-leachable with distilled water or a neutral leaching medium. However, under acid (and, sometimes alkaline) conditions, these metals will be resolublized and become available to the environment through leaching. If the actual ground water conditions are slightly acid, then the solidification process should be chosen so that the metals will not be leached under these real conditions. In addition, it may be necessary to choose the disposal site to properly protect the environment from extremely toxic constituents which might be leached out either normally or under changing ground water conditions. One of the worst examples of mismatching of wastes, solidification process, and disposal site has been the past practice of dewatering certain toxic metal hydroxide sludges, especially those from electroplating, and subsequently land filling the unfixed sludge into a sanitary landfill where the leachant generated by biological processes in the landfill is known to have a strong solublizing effect on metals and metal compounds.

Medium

The medium in which the waste constituents are dispersed is either water, an organic of some sort, or a combination of the two. Most processes used today are designed to work on water base systems, or on emulsions in which the liquid organic, such as oil, is reasonably well dispersed in the water medium. Pure solvent systems and inverse emulsions generally do not solidify well with the inorganic systems.

Physical Properties

The physical properties of a waste have a significant effect on the process used and on the proper formulation of that process. The primary properties which affect the system itself are solids content, particle size distribution and shape, viscosity and specific gravity. It is generally desirable to have high solids content because this will normally require smaller amounts of chemicals to be added, provided that the system does not itself react with the solids. Particle size distribution and shape in sludges have effects on the mechanical properties of the solid producted in the solidification process, as well as on the handling characteristics of the waste solution or slurry. For example, certain fibrous wastes may appear to be nearly solid at concentrations of only a few percent in water. On the other hand, flyash slurries can be pumped at solids concentrations of 60 to 70 percent because of the smooth, spherical shape of the flyash particles. Specific gravity and viscosity due to factors other than particle size and shape are also very important in choosing the solidification system, because in all cases the chemicals must be mixed into the waste (or vice versa), and the equipment and energy required to do this is dependent upon these physical characteristics. From the materials handling and energy standpoint it is desirable to be able to process and transport wastes by means of pumping and low energy mixing if possible, but the physical properties of the waste may require other means of conveyance and high energy mulling or blending.

A word here about viscosity. Most wastes which will be handled in solidification systems exhibit non-Newtonian rheological properties (viscosity is not independent of the rate of shear). As many truckers have experienced to their sorrow, a load of apparently solid filter cake can, under the shear stress set up by vibrations of the truck, turn into a fluid which will either pour out of the back of the truck or be deposited on the windshield and hood when the driver comes to a quick stop. This kind of situation occurs with plastic and pseudoplastic materials; i.e., the viscosity decreases with increasing rate of shear. Thus, many solid appearing sludges can be pumped quite easily once sufficient shear force has been applied to decrease the viscosity.

On the other hand, there are certain materials called "dilatant" which demonstrate increasing viscosity with increasing rate of shear and, as can be imagined, cause no end of problems for pump manufacturers since a sludge can literally turn solid inside the pump. Finally, certain materials are thixotropic; i.e., the viscosity of any particular rate of shear will depend upon the amount of previous shearing the waste has undergone - in other words, this waste has a memory. Thixotropy occurs as a result of the reversible gel-sol-gel transition, and is caused by the building up of a definite structure within the waste; the word "thixotropy" is often misused to describe all the other non-Newtonian flow characteristics.

Chemical Properties

It is obvious that the chemical nature of the waste should affect a solidification process; however, the number of possible interactions between ingredients of the waste and ingredients of the system are very large, very complex and often not completely understood. Basically there are three types of chemical interactions between the waste and the system which affect the solidification aspect of the system. (The detoxification or "chemical fixation" aspect is affected by different parameters). These are:

- Inhibition
- Acceleration
- Biological Activity

Perhaps the best examples of both inhibition and acceleration occur in the Portland cement processes, primarily because a great deal is known about the chemistry of Portland cement. Examples of inhibitors setting and hardening include boric acid and borate salts, various organic compounds, silt, coal, lignite, and a number of inorganic salts and metal compounds. Accelerators for Portland cement setting and curing include calcium chloride and sodium silicate. All of the processes will be affected by some reactive waste constituents, either in a positive or negative fashion. However, all inhibitors are not necessarily detrimental, nor are all accelerators desirable. It depends on how the system is to be used and upon the desired rate of setting and curing.

Biological activity in the waste causes problems in many systems. For example, in a biologically active organic sludge, cycling is sometimes seen between aerobic and anaerobic states, as evidenced by the evolution of hydrogen sulfide and by the obvious presence of various organic sulfur compounds. It is found with certain systems that the waste will harden when in one state, but not in the other (or hardening will be greatly retarded). Usually the aerobic state is the most desirable, but not always.

Working Hazards

In applying the solidification system, we are quite concerned about the health hazards associated with handling the waste and operating the system. Common hazards encountered are: inhalation toxicity due to vapors, dermal toxicity (skin irritation), corrosiveness (both to humans and to equipment), exothermic reactions (especially occurring during the mixing of the solidification chemicals with the waste), infection from biological wastes (especially sewage sludge), and unpleasantness associated with foul smelling wastes. These problems can all be managed properly by the use of protective equipment such as goggles, masks, protective clothing and inhalators, and by proper equipment design.

THE WASTE SOURCE

A common mistake in evaluating solidification processes is to consider only the interaction of the waste, the process and the disposal site, and to ignore problems associated with the generating or holding facility from which the waste will come. While these considerations most often affect cost, in some cases they can dictate the choice of the solidification system, the disposal site, and even have a determining influence on whether or not solidification technology is the proper approach. Some of the factors involved include:

- Holding Facility - size, age, condition, physical geometry, accessability, availability of utilities, climate.
- Transport of solidification equipment - distance, topography, obstacles (railroad tracks, roads, pipelines, etc.), necessary delivery rate, type of transport system (pump, conveyor, pipeline, etc.).
- Process Mode - continuous, semi-continuous, batch.
- Effect of plant stoppage on system, and vice versa, etc.
- Waste Removal System - dredge, pump, drag line, clam shell.

THE TREATMENT PROCESS

Following are the design parameters which must be considered in the choice of a solidification system:

- Chemical and operational cost for the process
- Type of system - fixed or mobile
- Capital write-off period (in the case of fixed systems)
- Required redundancy - for back-up
- Space requirement
- Labor and personnel considerations
- Occupational health considerations - dust, noise, toxicity, etc.
- Throughput rate
- Waste feed system
- Mixing system
- Chemical storage requirements
- Chemical feed system
- Utility and power requirements
- Setting and curing times
- Handling of solid after solidification
- Volume increase in the waste to be disposed as a result of the process.

A primary consideration, of course, is cost and this will affect, and be affected by, the type of treatment system used - for example, whether it is a fixed or mobile operation, the necessary write-off period on equipment in the case of a purchased fixed system, redundancy requirements to assure that operation of the plant or process line is not affected by the waste disposal operation, and space and labor required to house and operate the unit.

Specific design parameters which are determined before selecting a system include: throughput rate of waste, type of mixing equipment required (which is a function of both the type of waste and of the solidification system itself), optimum size of the chemical storage required, design of the chemical feed system (especially the accuracy required), matching of the chemical feed system with the waste feed system, and, finally, the utility and power requirements for the unit. In a continuous system the throughput rate will be determined as a function of the maximum output rate of the plant unless sufficient surge and holding capacity can be installed to average out the rate and not require maximum design. Requirements for chemical storage depend both upon the throughput rate and upon the chemical pricing and delivery situation in the specific locality. In the case of mobile treatment systems, the throughput rate is also of considerable importance. If the waste cannot be delivered to the mobile unit at a high rate, the economics of the system compared to other possible mechanical set-ups will be affected. The opposite effect occurs in the case of lagoons where the output rate of the dredge is substantially higher than the input rate of the solidification system. In this case, if dredging is hired as an outside service, the cost per gallon of material dredged will be higher than normal. Accuracy of the chemical feed system, especially with dry chemicals, is of importance since the more accurate the system the higher the capital cost. This must be balanced against the possible cost savings in chemicals by being able to achieve better control of the feed rates. The utility and power requirements are important, especially in remote locations where it may be necessary to supply power by means of motor generator units and to truck in water for both process and clean-up requirements.

The next group of process considerations concern the solid produced. In most cases a solidification area must be provided and its size will depend upon the solidification time required. In general, the longer the setting and/or curing time, the larger the temporary holding requirement. We also must determine whether the treated waste is to be solidified directly into a permanent disposal site, or transferred after solidification.

Last, but certainly not least, is the question of volume increase associated with the solidification process. Surprisingly, this factor, which is one of the most important of all in selection of a process, is usually neglected entirely in discussing solidification systems. This is probably due to the fact that most work has been done in on-site situations where the cost or value of the landfill space is either not considered or is believed, incorrectly, to be so insignificant as to have little bearing on the choice of systems. In the future, volume increase may be the most important single factor in choosing the system, because the value of landfill disposal space, especially for chemical waste, has been rising at a very rapid rate and this is likely to continue for some time.

THE DISPOSAL SITE

Most solidified wastes are disposed of in landfills, although there are situations in which the solidified waste may not be landfilled, as for example when it is stored for possible future recovery or other use, used for road base, or ocean-dumped. The following factors are considered by SolidTek and discussed with the customer and the regulatory agency before the system choice is finalized:

- Distance from the waste source.
- Location with reference to industrial and residential areas.
- Geology and hydrology.
- Available capacity.
- Disposal cost per ton or cubic yard of waste disposed.

- Overall envoronmental impact on the surrounding land, water and air.
- Attitude of neighbors, and general political considerations.
- Land use regulations (zoning, etc.)
- Liability and insurance considerations.

In the case of large waste volumes, it is often advantageous for the generator to use a single source landfill site on his own property, where he can exercise long term care and control free from many of the problems and unknowns associated with central disposal facilities. Also, on-site disposal is often more economical in the case of large quantities of solidified material. On the other hand, it is frequently not possible to accomplish on-site disposal because of lack of space, improper hydro-geological conditions, and other factors.

ENVIRONMENTAL IMPACT

This, of course, is the ultimate test of the proper application of a solidification/fixation system to a hazardous waste. The word "stability" is used with great frequency in discussions of solidification technology. But how do we determine stability? In fact, there are only three ways of determining the long term stability of solidified waste, or for that matter, of any other material. These are:

- Accelerated testing - designed to speed up the natural processes which might be involved in degradation of the material so as to simulate the results at any point in time in the future.
- Actual environmental testing - placing the solidified material into real and actual environmental conditions for the period of time constituting its expected life.
- Chemical modeling - determining the life time of the material by means of "paper" analysis of the chemistry of the system and its relationship to other systems of know stability.

Since we expect the solidified waste to be stable for an indefinite, and infinite, period of time it is obviously not possible to run actual environmental tests before such systems are put into commercial use. There are many accelerated tests developed for other types of materials which could be applied to solidified wastes; however, no standards have yet been set in this area. While various physical tests have been run on solidified wastes, most accelerated testing has been involved in determining leaching characteristics which are primarily associated with toxicity rather than with physical stability.

If the products formed from the chemical reactions involved in the solidification process are thermodynamically and kineticly stable under normally encountered ambient temperature conditions, we need concern ourselves only with other environmental factors such as ground water activity, wind and rain erosion, biological degradation and the effects of ultraviolet radiation. If the solidified waste is to be buried or covered, as is normally the case, then erosion and the effects of ultraviolet radiation are not very important; the primary factors are the effects of ambient ground water and biological degradation, and the latter is only a problem in certain solidification processes.

If ground or surface water passes through a material, each constituent dissolves at some finite rate. Even in the most impermeable solidified waste - or clay, concrete, brick or glass for that matter - water will eventually penetrate if there is a driving force. And wherever pure water penetrates, some of the waste dissolves; there is no such thing as an insoluble material. Therefore, when a waste, treated or not, is exposed to water we can measure a rate of dissolution.

Leaching is a rate phenomenon and our interest, environmentally, is in the rate at which hazardous or other undesirable constituents are removed from the waste and thus contaminate the leachant. This rate is usually measured and expressed, however, in terms of concentration of the constituent in the leachate because concentration determines its effects on living organisms, especially humans. (There are also, of course, cumulative effects determined by total exposure). Concentration is the primary regulatory basis for water quality standards, and water quality standards, especially drinking water standards, are presently the basis for leaching standards. Thus we talk about the leaching "rate" of a constituent, but usually mean its concentration in the leachate.

When evaluating a material for leachability, we usually compare the concentration of the hazardous constituent in the leachate to that in the original waste. This tells us what proportion of the constituent dissolved out during the test. If we can express the test conditions in terms of a time-related number, such as equivalent years of field exposure to rainfall, then we can express leachability in true rate terms; for example, pounds of constituent per year or % of original quantity per year.

Knowing the concentration in the original waste and the total quantity of the waste tells us something more - the potential hazard posed by that waste. As the hazardous constituents leach, the potential hazard gradually diminishes. If the leaching rate is such that the leachate is non-hazardous, then the leaching process is actually beneficial. This gives rise to the school of thought which says that a totally non-leaching waste deposit is a "time-bomb" that is not being "defused" with time and is therefore less desirable than a controlled leaching situation.

While considerable controversy still rages over how leaching tests should be run and with what leachants, much of the basic protocol for running different kinds of tests has already been established. Whether running a flowthrough, dynamic, column or lysimeter test, or a static, equilibrium, shakertype test, or the EPA Extraction Procedure, it is possible to make measurements which allow extrapolation of the leaching characteristics of the material into the future with a good probability of accuracy in predicting what the results would be under a given environmental condition. The real problem is in knowing what the actual field conditions are so that accurate test conditions can be formulated. Perhaps the best illustration of this problem is in the co-disposal of solidified industrial waste with domestic refuse in a sanitary landfill: in spite of all the work which has been done in this area, there is a little agreement as to what constitutes a meaningful leaching test for co-disposal.

At present, the leaching tests which are of importance from a regulatory stand point are:

- EPA EP Toxicity Procedure, 40 CFR Part 261.24
- ASTM Proposed Method A Water (or Acid) Shake Extraction Procedure

The EPA test is the acceptance test at the moment, but ASTM is developing standards which may come into use at a later time.

To date the only generally accepted performance standards for judging the results of a leaching test are those given in 40 CFR Part 261.24 along with the test specification. Unfortunately, these standards cover only a small part of the hazardous constituents spectrum. The same logic as was applied in 40 CFR Part 261.24 may be applied to other hazardous constituents in the future; i.e., 100 times the Drinking Water Standards or the Water Quality Standards for Human Health. Under the Clean Water Act, Human Health Standards have been developed for some 80 constituents for which there are no Drinking Water Standards. Since these Human Health Standards are at least as severe as the Drinking Water Standards (which were drived from them), this logic seems justified and has been accepted by state agencies in several instances to date. It is important to distinguish these standards from the aquatic life standards or the discharge standards under the NPDES permit system; most landfilled wastes directly affect groundwater quality, not surface waters, and groundwater quality normally affects human health, not aquatic life. In exceptional cases, where the landfilled waste directly impacts surface water, discharge standards should be considered.

An example of the results from running the EPA - EP Test on a chemically solidified waste pickle liquor is given below for an actual solidification operation (Table 1). The concentrations of contaminants in the leachate from both laboratory and field solidified samples are compared with the concentrations in the untreated waste.

TABLE 1. EP LEACHING TEST

Constituent	Concentration of Constituent in Untreated Waste mg/L	Concentration of Constituent Leached From Solidified Waste mg/L	
		Laboratory	Field
Arsenic	0.140	0.0013	0.5
Barium	27.4	3.17	0.22
Cadmium	2.91	0.054	0.021
Chromium,Total	15950.	0.364	1.00
Chromium,hexavalent	6.86	--	--
Lead	88.8	0.50	0.399
Mercury	0.260	0.0017	0.003
Selenium	2.6	0.0007	0.006
Silver	7.28	0.080	0.021

PRESENT-DAY SOLIDIFICATION SYSTEMS

Solidification and/or chemical fixation systems can be divided into three basic types: non-chemical systems, such as absorption; inorganic systems; and organic systems. These terms refer to the method used to produce fixation and/or solidification and not to the condition of the waste residue itself. Non-chemical, absorption-type systems are not chemical solidification/fixation but rather a separate technology which has other uses. Consequently, this discussion will center around inorganic and organic chemical systems, and primarily the inorganic systems, since these are the really well-proven systems that have been developed and used to date.

INORGANIC SYSTEMS

Inorganic chemical solidification and fixation systems which have been either used or proposed for use include:

- Portland cement
- Lime-Pozzolan (lime-flyash or lime-kiln dust)
- Lime-clay
- Lime-Portland cement
- Portland cement-sodium silicate
- Flyash-sodium silicate
- Soil-lime
- Portland cement-flyash (or kiln dust)

Many of the various permutations and combinations of these systems, including various types of additives, are patented or are covered with patents applied for.

The most important systems at the moment are lime-pozzolan, Portland cement-pozzolan, Portland cement-lime and Portland cement-sodium silicate. In volume of waste treated, the lime-flyash process has probably been the most used, although it has been narrowly applied primarily to flue gas desulfurization sludges. For other types of wastes and industrial sludges, the Portland cement based processes are the most widely used at the present time. These types of processes have been applied to a variety of wastes and a reasonably good technical base, including leaching test information, is available. The cement-flyash process works well with certain types of waste but, like the lime-flyash process, involves very large additions of the solidifying agents and therefore very large volume increases - a characteristic which is generally undesirable in a solidification system. The Portland cement-sodium silicate type process usually involves moderate volume increases but does not make use of waste products such as flyash which can be obtained inexpensively. In summary, the inorganic systems are characterized by:

- Relatively low cost
- Good long-term stability, both physically and chemically
- Documented use on a variety of wastes over at least ten years
- Wide spread availability of the chemical ingredients
- Non-toxicity of the chemical ingredients
- Ease of use in processing (ambient temperature and pressure)
- Relatively low volume increases with some of the processes
- Inertness to ultraviolet radiation
- High resistance to biodegradation
- Low water solubility
- Relatively low water permeability

- Good mechanical and structural characteristics

ORGANIC SYSTEMS

With the exception of processes for the incorporation of waste residues into liquid bitumen, or gross encapsulation in polyethylene jackets, organic systems consist of monomers or prepolymers which are polymerized or cross linked by the use of catalysts or accelerators after being mixed with the liquid waste. This kind of system is almost infinite in potential variety, but for practical purposes has been limited so far to the following:

- Urea-formaldehyde
- Polybutadiene
- Polyester-epoxy
- Acrylamid gel
- Urea-formaldehyde with plaster of paris
- Polyolefin encapsulation
- Bitumen asphalt
- Polyurethane

Many combinations of the above and of other organic polymer systems are conceivable. In most cases, the action of the organic polymer is primarily permeation limiting. Usually there is no direct reaction between the waste constituents and the polymer, nor does the system actually insolublize, detoxify, or destroy the hazardous constituents. The mechanism of most organic systems is microencapsulation of the waste material, which separates the wa[illegible] from its environment. In summary, the characteristics of organic systems are

- High cost
- Very low permeability
- Potential of using one system with a wide variety of wastes
- Wide range of volume increase
- Relative instability in the presence of ultraviolet light
- Questionable stability in the presence of microorganisms
- Potential long term degradation effects on the polymer matrix by certain waste constituents
- Unproven long term stability even in the laboratory
- Very limited commercial use experience except with radioactive waste.
- Systems are more difficult to use and require more technical expertise.
- Some system components, especially catalysts, initiators and accelerators, are hazardous.

PROVEN SYSTEMS

Only the inorganic, siliceous-base systems presently have the track record necessary for safe and reliable solidification of wastes which are ultimately to be disposed of other than in a (RCRA) Subtitle C land disposal facility. In particular this is the case where hazardous waste, either listed or unlisted, is to be detoxified to allow its safe and proper disposal in a Subtitle D facility, or in any other landfill operation which does not meet secure landfill criteria. The basic chemistry of these systems is the same as that of rock, clay, concrete, brick, glass and other such materials which are known to be the most stable physical forms on earth. They are not affected by ultraviolet radiation, they are non-biodegradable, and they have a very high degree of resistance to ground or surface water. Because of these characteristics, and our knowledge of the kinetics and thermodynamics of these materials, it can be expected that properly formulated solidification systems such as these change only very slowly in the ground - on the same time scale as natural rocks and minerals. The possibility of a sudden or catastrophic change in such materials is almost non-existent.

In addition to the basic siliceous components of the chemical solidification system, various minor component additives are used to adapt the basic systems to the particular waste being used and also to the processing mode in which the solidification is to be carried out. Also, additions may be made to insolublize and precipitate specific waste components, especially the toxic metals. The insoluble form of the constituent is then entrapped in the inorganic polymeric matrix and completely immobilized thereafter.

Chemical solidification/fixation systems have been successfully applied to the following wastes from the iron and steel industry (Table 2).

TABLE 2. IRON AND STEEL WASTES TREATED

EPA Number	Waste
K062	Emission control dust/sludge from the electric furnace production of steel
K062	Spent pickle liquor from steel finishing operations
--	Cupola dust
--	Scale pit sludge
--	Neutralized waste pickle liquor
--	Wastewater treatment sludge
--	Metal fines
--	Waste pickle liquor sump sludge.

COSTS

Typical cost ranges for the various operations involved in a complete disposal system based on CF/S are as follows:

TABLE 3. UNIT OPERATIONS COSTS

	Cost-$/gallon
Dredging	.0025-.05
Solidification	
Commercial Processes(non-nuclear)	.05-.45
All Processes	.05-2.75
Transportation	
Solids	.01-.30
Liquids	.03-.50
Landfill	
Non-Secure	.01-.20
Secure	.20-3.00

As can be seen, transportation and landfill costs can vary through a very wide range. Transportation cost is primarily dependent on distance, and can be readily determined on a "typical case" basis. Landfill cost on the other hand, depends on many factors and can be accurately determined only by specific quote. Dredging costs are site specific.

For comparative purposes, cost ranges for various commercial treatment and disposal alternatives are:

TABLE 4. COMPARATIVE COSTS

	Cost-$/gallon
Chemical Fixation/Solidification*	.05-.45
Direct Landfill or Land Spreading	.02-.20
Secure Landfill	.20-3.00
Incineration	.20-5.00+
Ocean Dumping	.01-.05
Ponding	.01-.05

*CF/S processing only.

OPTIMIZING EXISTING WASTEWATER TREATMENT FACILITIES IN PREPARATION OF MEETING BAT/BCT REGULATIONS IN THE IRON AND STEEL INDUSTRY

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ABSTRACT

This paper discusses the impact of the BAT/BCT regulations on existing central treatment facilities. In order to prepare for these new regulations it will be necessary to review the origin of the waste sources and install pretreatment facilities or internal recycle loops to minimize the cost of end of the pipe treatment schemes. The three examples reviewed in this paper are for a hot mill, a cold mill and a by-product area.

INTRODUCTION

As a result of various pollution control laws the iron and steel industry has built several wastewater treatment systems in the various areas of an integrated steel mill over the last few decades. These systems were built as a result of state regulations or of the federally enacted BPT regulations. Most of the facilities were built using the treatment concepts available at that point in time. This often resulted in centralized treatment facilities that were constructed to handle a variety of waste streams. With the upcoming BAT and BCT regulations it might be difficult to add end-of-the pipe treatment technology to these central facilities in order to meet these new regulations. Therefore, it could become necessary to go back to the source and install pretreatment systems or implement recycle loops. Generally, the approach of going back to the source has an added advantage in that it will make the operation of central facilities often easier and more reliable because of the elimination of potentially incompatible waste components.

By reducing the flow rate and/or pollution loading to the treatment facility the cost for any additional end of the pipe treatment unit operations will be kept to a minimum. This paper will discuss three examples of three areas in an integrated steel mill where central facilities were used and how these could be upgraded to prepare for the BAT and BCT regulations. The three areas to be discussed will be: 1) a Hot Mill Area, 2) a By-Product Area, and 3) a Cold Mill Area.

HOT MILL AREA

The schematic of the Hot Mill area to be used as an example in this paper is presented in Figure 1. The various waste sources from these Hot Mill operations are 1) non-contact cooling water that was not segregated, 2) flume flush water, 3) roll cooling water, 4) descaling water, 5) scarfer water.

The major contaminants of concern for the BPT regulations are the suspended solids and the oil and grease. A typical treatment concept for this type of operation is also shown in Figure 1 and consists of a scale pit for removal of heavy solids to protect the sewers and pumps and a clarifier for the removal of the residual solids and free oil. With good operation of the treatment facilities and reasonable water consumption it is possible to meet the BPT regulations with such a scheme. The BPT and BAT/BCT limits for the operations included in this example are shown in Table 1.

TABLE 1. BPT AND BAT LIMITS FOR HOT MILL AREA

Parameter	BPT	BAT/BCT*
	Total lb/day	Total lb/day
TSS	9850	690
O&G	4820	460**
Chromium	-	4.6
Lead	-	4.6
Zinc	-	4.6

* TSS and O&G are covered by BCT, cr, pb and Zn are covered by BAT

** Maximum at any one day

The flow rates from these four mills are shown in Table 2. In each of these areas there is a potential for flow reduction at a certain cost. Because of the lack of incentive in the past about strict flow segregation, there is presently still some noncontact cooling water entering the treatment system. Also, flume flush recycle was not a necessity and therefore it was never implemented. For comparison also the flow rates that should be met according to EPA's Development Document are shown. The table shows that the total existing flow is about 50,000 gpm. With some capital cost it is possible to reduce the flow rate to the existing facility to about 30,000 gpm by segregating non-contact cooling water and recycling flume flush water after the scale pits. With the design flows EPA is using for its models, the total flow to this facility would be 40,000 gpm which shows that it is possible for the existing facility to meet the BPT limits. However, with the BAT/BCT regulations the flow rate to be discharged from the central facility is supposed to be not more than 4,000 gpm. This means that in addition to the segregation and flume flush recycle this facility would have to recycle about of 80 to 90% of the effluent.

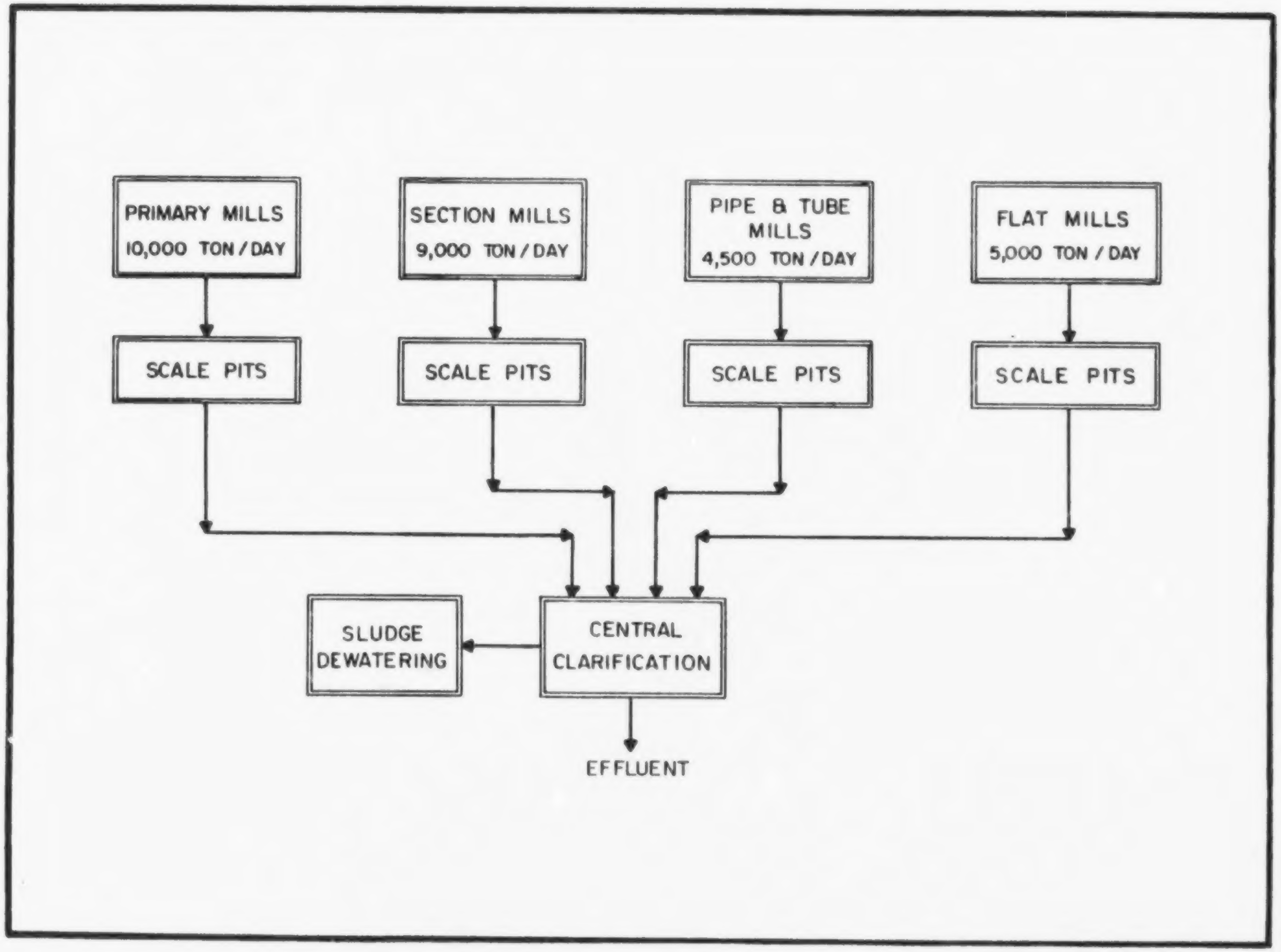
PRIMARY MILLS
10,000 TON / DAY
SECTION MILLS
9,000 TON / DAY
PIPE & TUBE
MILLS
4,500 TON / DAY
FLAT MILLS
5,000 TON / DAY
SCALE PITS
SCALE PITS
SCALE PITS
SCALE PITS
SLUDGE
DEWATERING
CENTRAL
CLARIFICATION
EFFLUENT

Figure 1. Hot Mill Area

TABLE 2. FLOW RATES HOT STRIP MILL AREA

Mill	Existing Flow gpm	Potential Future Flow gpm	EPA Discharge Flows BPT gpm	EPA Discharge Flows BAT/BCT gpm
Primary	14,000	11,000	6,500	1,100
Section	16,000	8,000	16,500	1,300
Pipe	13,000	3,000	3,100	800
Flat	8,000	8,000	14,500	800
Total	51,000	30,000	40,600	4,000

The effluent limitations are not dictating the treatment technology to be used. The effluent regulations are expressed in mass discharge limitations as shown in Table 1. For the flows shown in Table 2 and the mass discharge limit in Table 1 it is possible to calculate the allowable concentrations in the effluent from the facility at different flow rates in order to meet the BPT and BAT/BCT limits. The results are shown in Table 3.

TABLE 3. NET CONCENTRATION DISCHARGE LIMITS AT VARIOUS FLOWS HOT STRIP MILL AREA

Flow Rate, gpm		Concentration, mg/l TSS	O&G	CR	PB	ZN
51,000	- BPT	16	8	-	-	-
	- BCT/BAT	1.2	0.8	0.0075	0.0075	0.0075
30,000	- BPT	27	14	-	-	-
	- BCT/BAT	2.0	1.3	0.013	0.013	0.013
40,600	- BPT	20	10	-	-	-
	- BCT/BAT	1.5	1.0	0.0094	0.0094	0.0094
4,000	- BCT/BAT	1.5	10	0.10	0.10	0.10

This table shows that:

1. The BAT limits for toxic metals become extremely low at high discharge flows. In case the limits are expressed on a net basis there is a good chance that the background metal concentration is higher than the limit. For example, Table 4 shows typical metal concentration in the Ohio River.

2. The BCT limits for solids can only be met by extensive recycling and/or filtration or a combination of the two, when the limits are expressed on a gross basis. If, however, the limits are on a net basis, the background solids content would allow a much less rigorous upgrading program and clarification could still be a viable alternative.

TABLE 4. TYPICAL HEAVY METAL CONCENTRATION IN OHIO RIVER

Parameter	Concentration, mg/l
Chromium	Not Available
Lead	0.010 - 0.020
Zinc	0.040 - 0.080

The BCT limits are supposed to have passed a "cost reasonableness test" which means that the cost for removal of the additional solids will be less than similar cost for a POTW which is $1.34/lb (1978 dollars). In this example BCT will remove an additional 3,300,000 lb of solids per year. This shows that quite an extensive facility has to be built before the cost will exceed this "test".

BY-PRODUCT AREA

The example for the By-Product area to be discussed in this paper is shown in Figure 2. The waste sources are indicated on the schematic. The major sources are waste ammonia liquor, preheater blowdown, final cooler blowdown and the blowdown from the benzol plant. Each of these sources in turn is the summation of several individual inputs. Therefore, while evaluating potential schemes for segregation and recycle it is necessary to review the contributors to each wastestream. For example, the water in the waste ammonia liquor originates from 1) coal moisture and hydrogen oxidation, 2) the lime slurry added to the fixed still, 3) ammonium sulfate crystallyzer blowdown, 4) condenser blowdown, 5) charging liquor, 6) various cleaning operations, 7) drainage from process operations and 8) steam condensate. In some plants a desulfurizer also is used which will again increase the flow rate.

Another potential source of wastewater in the By-Product area is the blowdown from various air pollution control devices. Figure 2 shows the blowdown of a coal preheater. This waste originates from a scrubber on a preheating operation. Other pollution control devices that could discharge a blowdown are from coke pushing control. Table 5 shows these major contributors and the flowrates according to EPA. The production of the example By-Product area is about 4,000 ton/day. The flowrates and the characteristics of the raw waste are shown in Table 6. The flowrate according to the EPA BPT model can be 225 gal/ton or a total of 620 gpm. The BAT flowrate is 153 gal/ton and this will result in an average flow of 420 gpm.

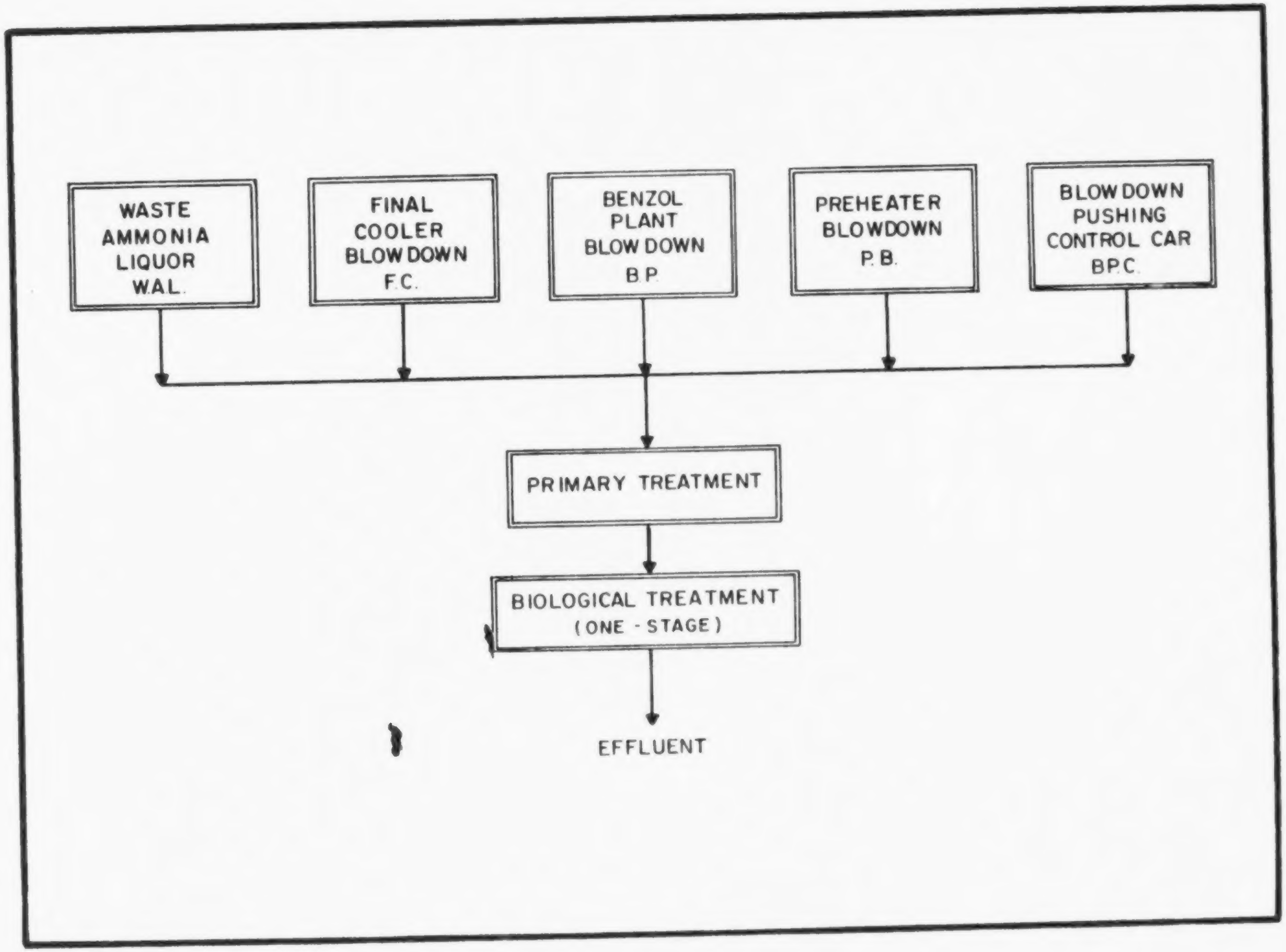
WASTE AMMONIA LIQUOR W.A.L.
FINAL COOLER BLOWDOWN F.C.
BENZOL PLANT BLOWDOWN B.P.
PREHEATER BLOWDOWN P.B.
BLOWDOWN PUSHING CONTROL CAR B.P.C.
PRIMARY TREATMENT
BIOLOGICAL TREATMENT (ONE - STAGE)
EFFLUENT

Figure 2. Coke Oven Area

TABLE 5. MAJOR WASTE CONTRIBUTORS COKE CATEGORY
REF: EPA DEVELOPMENT DOCUMENTS

	Flow gal/ton Range	Flow for Example 4000 ton/day in gpm
Ammonia Liquor	21 - 49	
Final Cooler Blowdown	2 - 10	
Benzol Plant	15 - 120	
Barometric Condenser (with recycle)	3 - 10	
Desulfurizer	12 - 30	
Preheater	3 - 15	
Pushing Control	5 - 25	
EPA - BPT Total Flow to Treatment Plant	225	620
EPA - BAT Total Flow to Treatment Plant	153	420

TABLE 6. FLOW RATES EXAMPLE COKE OVEN AREA

	Flow	Characteristics,* mg/l			
Source	gpm	Phenol	Ammonia	CN	SCN
Waste Ammonia Liquor	200	500	150*	15	200
Final Cooler Blowdown	100	200	100	100	200
Benzol Plant Blowdown	110	100	50	20	150
Preheater Blowdown	120	10	25	-	-
Pushing Control Blowdown	40	5	5	-	-
Total	570		86	27	136

*Concentrations after WAL and FCB pass through ammonia still.

As in any other system the lower the total flowrate the easier it will be to meet the EPA-BPT and BAT/BCT guidelines. Table 7 shows the EPA effluent guidelines for the coke making sub category. Table 8 shows the concentration limits for the EPA models and the example.

TABLE 7. EFFLUENT GUIDELINES COKEMAKING SUBCATEGORY

Parameter	BPT		BAT/BCT*	
	lb/100 lb	lb/day	lb/1000 lb	lb/day
TSS	0.0750	600	0.0128	102
O&G	0.0109	88	0.00638**	51
NH_4-N	0.0912	729	0.00957	77
CN	0.0219	176	0.00160	13
Phenols	0.0015	12	0.0000160	0.13
Benzene	-	-	0.0000319	0.25
Napthalene	-	-	0.0000064	0.051
Benzo pyrene	-	-	0.0000128	0.10
Flow, gal/ton	225	-	153	-

* TSS and O&G are covered by BCT, other parameters by BAT
** Maximum any one day

TABLE 8. CONCENTRATION LIMITS

Parameter	Flowrate gpm			
	EPA		Example	
	BPT - 620	BAT-420	BPT-570	BAT-410
TSS	80	21	87	21
O&G	12	10	13	10
NH_4-N	97	15	106	15
CN	23	2.5	25	2.5
Phenols	1.6	0.025	1.7	0.025
Benzene	-	0.025	-	0.05
Napthalene	-	0.01	-	0.01
Benzo Pyrene	-	0.02	-	0.02

The example used shows that with the existing system the BPT limits can be met with a single stage biological treatment facility. The incoming ammonium concentration in the 570 gpm is 86 mg/l. In addition to this, the biological breakdown of cyanide and thio-cyanate will also result in ammonium. The total equivalent ammonium input is about 125 mg/l. As shown in Table 8 the effluent limitation is 106 mg/l. It is very likely that the effluent limit will be met because of the ammonium utilization for cell production. The effluent phenol limit is 1.7 mg/l. Normally phenol is a readily oxidizable material and it should be possible to meet this concentration with a single stage biological system. With the BAT guidelines, however, it will be necessary to expand the facility to incorporate provisions for nitrification. It generally is possible in a by-product area to reduce the flow rate to the treatment plant in various ways. This flow reduction would help in meeting the effluent limitations since it will be difficult to remove the ammonium to concentrations consistently less than 10 mg/l. In the example for this category it is proposed to use the wastewater from the coal preheater and from the pushing control blowdown for quenching because of the low salt concentration in these waste streams. Only an extensive plant survey can reveal whether the other flows can be reduced substantially. Generally, ways of doing this are: 1) replace barometric condensers with surface condensers, 2) use recycle water for lime slurry makeup, 3) bypass clean water streams directly to the quench sumps, 4) use recycle water as much as possible for cleaning operations, 5) keep rainwater out of the system, 6) use recycle water for fines dissolution in the ammonium sulfate crystallyzer, 7) use recycle water for the charging system. The benefit from reducing the hydraulic loading to the plant will be a more realistic ammonium concentration limit that can be met consistently and a reduced hydraulic design.

The BCT guidelines will have little effect on the required facility although the solids effluent limitation of 20 mg/l is rather tight and requires excellent clarifier performance. In some cases filtration may be required.

COLD MILL AREA

The schematic of the sources and the treatment concept for this area is shown in Figure 3. Table 9 indicates the individual flowrates and waste characteristics from each of these major waste sources. In a central facility like this, it is very difficult to treat each of the components to the largest extent possible since it is almost impossible to fine tune the large facility for each of the several parameters that have to be removed. For example, the oil and grease from the tandem mill and from several oil cellars can be removed to the extent that a provision is made to remove any free oil and to the extent that soluble metal ions in the water can break emulsified oil. However, this type of removal is coincidental and no firm control can be exercised on this removal. Furthermore, the waste sources from these various areas will vary from time to time and it is impossible to rely on certain waste sources to be always present to treat the other components. In other words, if the influent to the treatment facility is more or less neutral the emulsified oil will not be removed and will pass through. The same is true for the hexavalent chromium from the tin lines. Again, hexavalent chromium is reduced by ferrous iron normally available in the rinsewaters from pickling lines. However, the removal again is incidental and is not a positive type of control since it is possible that the chrome is discharged while the pickling lines are not operating. Also, the pH of the influent could be unfavorable for this reaction and therefore the facility will result in inadequate chrome reduction.

The BAT guidelines for a facility like this are very difficult to determine. For the tin lines EPA has not yet proposed BAT guidelines and the contribution from the boilerhouse will never be subject to BAT. Therefore, this section cannot be very specific about the actions to be taken to meet the BAT guidelines. However, a few examples can be presented on the approaches available. For example, if a fluoride limit is set on the discharge from the tin lines then it probably will be needed to segregate the

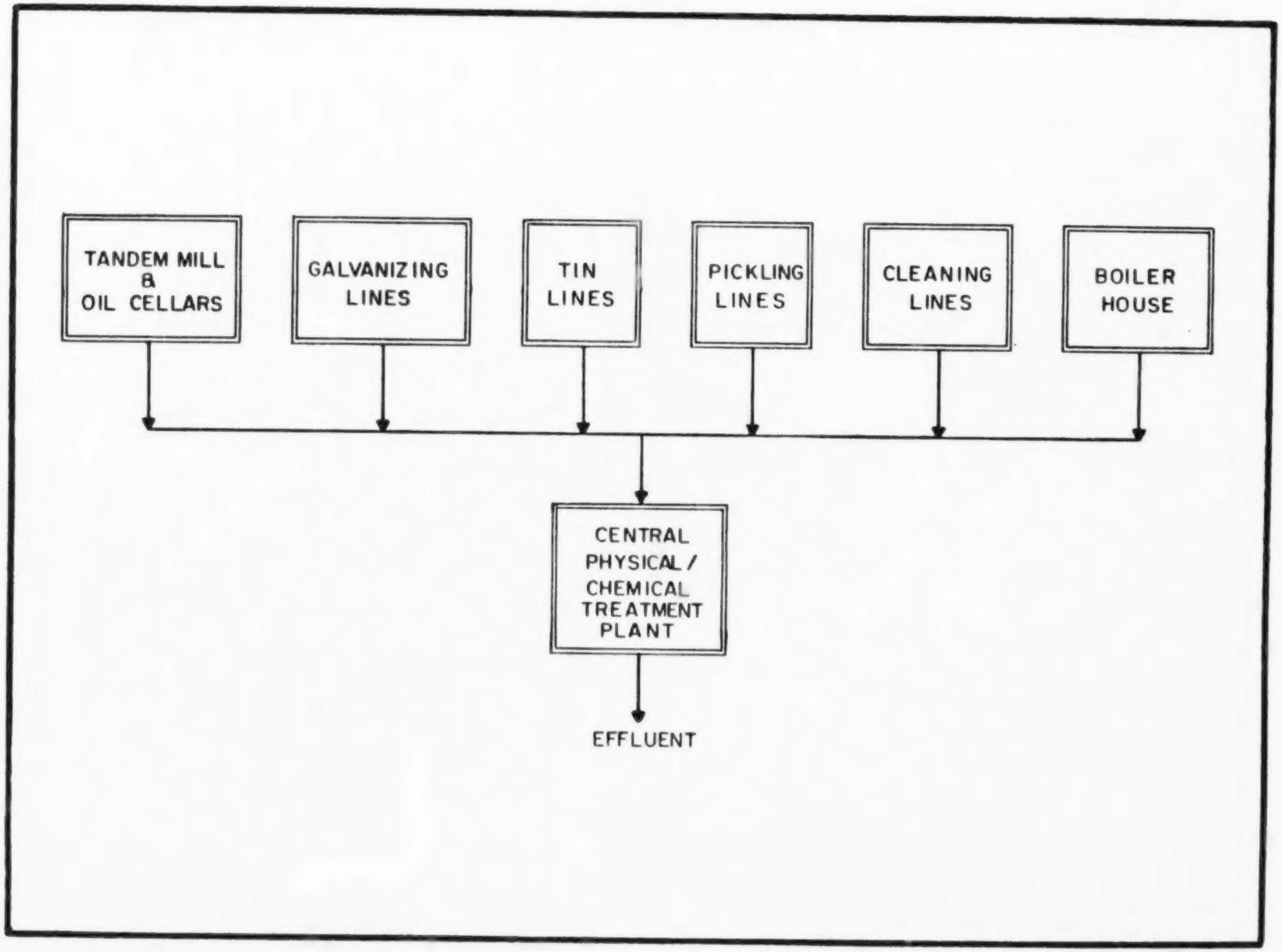
TANDEM MILL
&
OIL CELLARS
GALVANIZING
LINES
TIN
LINES
PICKLING
LINES
CLEANING
LINES
BOILER
HOUSE
CENTRAL
PHYSICAL/
CHEMICAL
TREATMENT
PLANT
EFFLUENT

Figure 3. Cold Mill Area

fluoride containing wastestreams and separate the calcium fluoride sludge from the segregated facility prior to dilution in the other wastestreams. Fluoride is only removed to its solubility limit of 15-20 mg/l. Once the raw waste is diluted the 20 mg/l in the total wastestream, it is probably beyond any BAT guidelines for tin lines. This approach might also have to be taken with the chromium containing rinsestreams from the tin lines. Again, treating hexavalent chromium in a large wastestream is expensive and requires a lot of chemicals plus the residual concentration will be met in a large wastestream. By segregated treatment it will be possible to meet this residual concentration in a much lower wastestream after which the dilution will virtually make it impossible to analyze for this contaminant. As far as the oil and grease is concerned it might be necessary to provide some pretreatment facilities for the tandem mill and the oil cellars. In this way the free oil can be recovered and possibly recycled, while the emulsified oil can be treated in a more positive way. In some cases it is possible to break these emulsions with organic polymers after which the oil can be recovered by flotation. However, in other cases it is necessary to add metal solids or waste pickle liquor to break the emulsion and the oil is lost.

In this area the BAT guidelines will become very difficult to apply and apparently EPA is realizing this by planning to make special provisions for central treatment facilities.

TABLE 9. CHARACTERISTICS WASTE SOURCES COLD MILL AREA

	SOURCE					
	Tanden Mill & Oil Cellars	Galvanizing Lines	Tin Lines	Pickling Lines	Cleaning Lines	Boiler House
Flow - gpm	350	130	750	250	350	225
Oil & Grease, mg/l	1000*	75	50	150	150	10
Suspended Solids	300	100	100	60	200	2,000
Iron	negl	100	20	75	negl	negl
Zinc	negl	200	negl	negl	negl	negl
Tin	negl	negl	100	negl	negl	negl
Chromium	negl	negl	75	negl	negl	negl
Fluoride	negl	negl	250	negl	negl	negl

*Almost 40% is emulsified oil

DEVELOPMENT OF A DEOILING PROCESS FOR RECYCLING MILLSCALE

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INTRODUCTION

The annual production of raw steel in the United States and Canada averaged 134 million tons over the last seven years. In that same period, the generation of iron-bearing waste solids reached a level of roughly 13 million tons,(1)* of which approximately 7 million tons were mill scale. This tonnage of mill scale constitutes 3.7 to 4.7 percent(2)* of the annual raw steel output of an integrated steel plant and is governed by operating practice, the types of steel produced, the availability of continuous casting, and overall mill facilities.

Among the various waste oxides produced in a steel plant, mill scale is the most attractive candidate for reclamation because of its high iron content and its potential for replacing costly purchased iron units.

Several different contaminants in varying quantities accompany the raw mill scale which is generated. Among these are metallic scrap, rubble, moisture, mill lubricants, and rolling oil, which are picked up during the various processing steps. These contaminants are tabulated in Table 1. The scrap and rubble can be removed mechanically, but the moisture and oil must be treated by other means for reduction or elimination. In general, the quantities of both oil and moisture increase with decreasing particle size.

TABLE 1. RAW MILLSCALE CONTAMINANTS

Scrap	Percent Range
Plus 5" Size	0.3 - 0.5%
+5/8" - 5"	2.0 - 3.5%
Moisture	3.0 - 9.0%
Oil	0.3 - 10.2%
Rubble	0.2 - 0.5%

*See references

Until recent years, mill scale under 1/4 inch in size was recycled to the sinter plant and contributed low cost iron units as well as enhanced the quality of the sinter produced.

At the present time however, with the advent of sophisticated air pollution control facilities, oily millscale cannot be sintered in large quantities because of mill operating problems and environmental restrictions. Oil contained in the millscale volatilizes during sintering resulting in a carryover of hydrocarbons to the bag house or scrubber. These hydrocarbons present a fire hazard, can blind the filter bags and result in unacceptable stack emissions. Removal of the hydrocarbons before sintering is therefore essential in order to achieve maximum recycling of this material.

The problems imposed by hydrocarbon contamination have caused substantial tonnages of oily mill scale to be stockpiled while significantly less desirable waste oxides have been recycled.

Several methods for oil removal have been investigated and are described in the literature.(2)* These processes are shown in Table 2. While each of these systems is attended by varying degrees of success, Luria chose direct incineration as both the simplest and the most likely to provide consistent success in removing oil from scale.

TABLE 2. MILLSCALE DEOILING METHODS(2)*

Washing	Thermal Incineration
1 - Water	1 - Direct Firing
2 - Hot Alkaline	2 - Indirect Firing
3 - Solvent	

The selection of direct incineration resulted in the construction of a plant in Gary, Indiana, for de-oiling mill scale generated at Inland Steel Company. This facility began operating in November, 1978.

PROCESS DESCRIPTION

Figure 1 shows the de-oiling plant layout and the flow path of the mill scale received from the steel plant.

Unprocessed mill scale is delivered to the facility by truck and weighed into the raw material stockpile. A front end loader equipped with a 4 yard bucket transports the material to the grizzly where scrap and rubble over 5" is removed. A pan feeder under the grizzly hopper controls the flow of mill scale to the conveyor travelling to the vibratory screen. Oversize material on the 5/8" x 2" screen passes to the magnetic separation equipment which recovers scrap suitable for direct charge to the blast furnaces. Rubble is collected at the end of the conveyor for disposal. Minus 5/8" x 2" screened mill scale from the vibrating screen moves by conveyor to the kiln

*See references

feed hopper which holds approximately 20 net tons. Delivery of oily material to the kiln is accomplished with a variable speed feed screw.

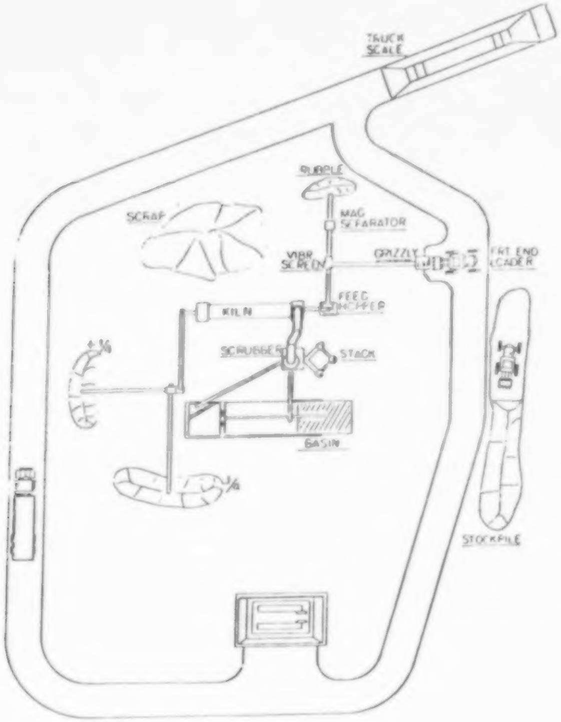
TRUCK SCALE
RUBBLE
SCRAP
MAG SEPARATOR
VIBR SCREEN
GRIZZLY
FRT END LOADER
FEED HOPPER
KILN
+¼
SCRUBBER
STACK
BASIN
-¼
STOCKPILE

Figure 1. Deoiling Plant

The rotary kiln is gas fired, 10' in diameter by 60' long and is lined with 6" of refractory lining. Oily mill scale entering the kiln is agitated by kiln rotation and internal lifters which cause the material to cascade through the hot combustion gases. The kiln rotates at slightly less than 4 RPM's with retention time of approximately 12 minutes.

Dry, oil-free scale is discharged from the kiln and conveyed to a vibrating screen which separates the plus 1/4-inch from the remainder for return to the blast furnace. Dust is suppressed by adding a small amount of water to the minus 1/4-inch material.

Table 3 describes the dry properties of the de-oiled mill scale and demonstrates that the iron-rich material is well within the residual oil limit of 0.01%.

Table 4 outlines the particle size distribution of treated scale which is recirculated to the sinter strand. The composition of the scale and its relative fineness result in a bulk density ranging from 190 to 205 pounds per cubic foot.

TABLE 3. DEOILED MILLSCALE ANALYSIS(2)*
SINTER PLANT SIZE (Dry Basis)

	Percent
Total Fe	76.2
Fe++	45.9
Fe+++	18.7
Metallic Fe	11.6
Magnetic Fe	26.3
Gangue	4.0
Sul	.029
Oil	.005*

*Oil Specification - .01% Max.

TABLE 4. PHYSICAL PROPERTIES DEOILED MILLSCALE(2)*
SINTER PLANT SIZE

Screen Size	Wt. %	Cum. Wt. %
Plus ¼"	0.4	0.4
- ¼" + 4 Mesh	1.0	1.4
- 4 + 6 Mesh	3.0	4.4
- 6 + 10 Mesh	8.8	13.2
- 10 + 18 Mesh	13.5	26.7
- 18 + 32 Mesh	28.4	55.1
- 32 + 60 Mesh	18.8	73.9
- 60 +100 Mesh	13.8	87.7
-100 Mesh	12.3	100.0

Bulk Density (Dry Basis) 190 - 205 lb./ft.^{3}

The oil-free and moistened mill scale is loaded from the product stockpile and transported to the sinter plant at Inland Steel, a distance of approximately 3/4 mile.

PRODUCTION RESULTS

Production of sinter plant size material has averaged 31,127 net tons per month for the past 30 months, with a best single month output of 38,575 net tons in December 1980.

Both delivery of raw scale and shipment of treated scale are normally made on a five-day per week basis. Thus, the average daily shipment of deoiled material to the sinter plant has been 1,480 net tons. See Table 5 below.

See references

TABLE 5. PRODUCTION STATISTICS

Year	Tons Shipped
1979	301,208
1980	373,658
1981 (Projected)	374,131

ENVIRONMENTAL RESULTS

The hot gases leave the kiln at a temperature of roughly 800°F and pass into an after burner chamber where the temperature is raised to about 1500°F for complete incineration of residual hydrocarbons. Approximately 25,000 cubic feet per minute of hot gases leave the after burner and travel through ductwork into a high intensity wet scrubber before being discharged into the atmosphere. The duct is refractory lined and the internal gas velocity is sufficient to entrain any particulate matter.

The wet scrubbing system is shown in Figure 2. Water is sprayed into the system at a rate of 400 gallons per minute and the pressure drop across the venturi throat is 20 inches of water. After being scrubbed and having particulates removed, the clean gas passes through a mist eliminator and then into the induced draft fan and the stack.

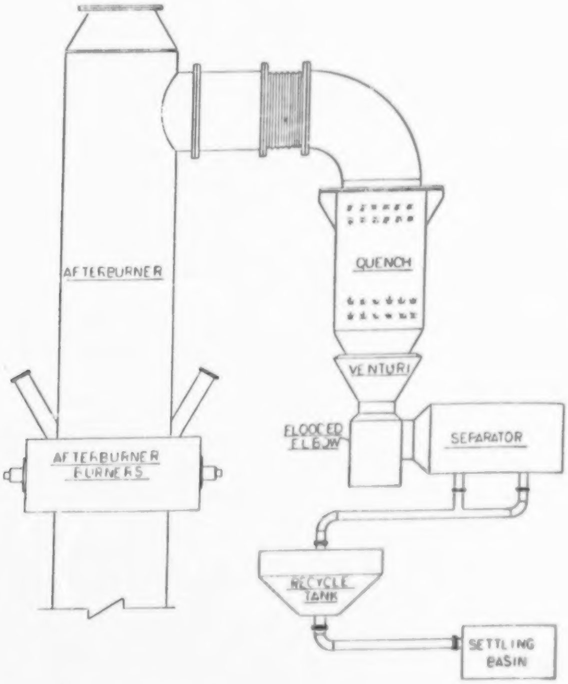

Figure 2. Wet Scrubber Elevation View

Based upon the fraction of solid matter removed, the scrubber efficiency is above 99%. The data are shown in Table 6. The system has performed with exceptional efficiency since operation began. The stack emission rate has been consistently under 2 lbs. per hour and is always substantially below the permissible level.

TABLE 6. WET SCRUBBER EFFICIENCY

Test	Production Rate	Scrubber Inlet Particulate Loading	Stack Particulate Emission Rate	Efficiency
#1	43 NT/Hr.	1280 lb./Hr.	1.8 lb./Hr.	99.8%
#2	43 NT/Hr.	951 lb./Hr.	1.3 lb./Hr.	99.8%

The slurry from the scrubber is pumped to a basin where the solids settle quickly, and the water is returned to the scrubber for re-use.

From a performance point of view, the scrubber has operated very well. Excessive abrasion and internal erosion, resulted in relatively high maintenance costs initially. Consequently, the quencher, venturi inlet, and venturi throat were replaced with more abrasion-resistant material. Experimental work with refractory coatings demonstrated satisfactory performance, and this material is being utilized for the internal parts which are subject to abrasion wear.

PROCESS COSTS

Process costs are most sensitive to fuel costs, and the steady rise of fuel oil prices prompted the immediate shift to natural gas when it became available in May 1980. This shift resulted in a 58% reduction in fuel costs and, together with improved handling methods and the employment of more abrasion-resistant construction materials, resulted in a deoiling cost significantly below $15.00 per ton including depreciation, SAG and profit.

CONCLUSIONS

The following conclusions may be drawn from Luria's work:

(1) Large quantities of oil-contaminated mill scale can be treated economically on a steady, high tonnage basis.

(2) The process produces material of consistently high quality and low oil content. These features insure operation of the sinter plant within the environmental standards established. Mill scale in the sinter mix is approximately 25%.

(3) Optimization of fuel selection, burner placement, and construction materials will provide a low cost source of valuable iron units, and will simultaneously minimize disposal and environmental problems.

FUTURE PLANS

It is recognized that the existing mill scale de-oiling plant is but a first generation facility, and that much can be done to make its operations more attractive.

To this end, a proposed 2nd generation plant incorporates the more wear resistant materials of construction as well as improved methods for handling and transferring a heavy, abrasive material. These improvements will result in 85% availability of the equipment and reduce maintenance costs to their lowest level.

In addition to the shift from fuel oil to gas, a program to study the effects of burner position within the kiln has been initiated. The placement of the burners within the after burner chamber will also be investigated for optimum results and fuel conservation.

A further program will be undertaken to determine whether the use of recuperators in the waste gas stream can provide an additional cost reduction which will warrant the required capital investment for such a system.

Long range considerations point to steady refinement of the process to achieve lowest possible cost in de-oiling mill scale. At the same time, the processing of other steel plant wastes is being examined to ascertain whether these less valuable but important materials can also be treated in the equipment in an acceptable manner.

Agglomeration process studies will also be pursued to establish the response of de-oiled mill scale and to determine whether the agglomerates can be returned to the blast furnace or steel plant directly, thus saving the cost of sintering.

The work already accomplished, as well as that being planned is vital. The recovery of iron, carbon, calcium and other valuable units is essential considering future availability and cost of these materials. Finally, reclamation and recycling of mill waste materials can eliminate or minimize in-plant handling, storage and environmental problems. We believe these concepts to be a very important support of a strong and prosperous Steel Industry in the United States.

REFERENCES:

(1) Harris, M. M., The Use Of Steel Mill Waste Solids In Iron And Steelmaking. American Iron and Steel Institute - 86th General Meeting, May 24, 1978.

(2) Balajee, S. R., Deoiling And Utilization Of Millscale. First E.P.A. symposium on the Iron and Steel Pollution Abatement Technology. November 1, 1979.

RECYCLING OF TAR DECANTER SLUDGE

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Tar is one of the saleable by-products derived from coke making. The tar is driven off from the coal in the coke ovens. It is collected, condensed and separated from the water phase in tar decanters. In 1979 the 2,276,143 tons of coal charged into the coke ovens yielded 12,672,928 gallons of tar or 5.6 gallons of tar per ton of coal. In the processing some of the tar becomes contaminated with solids, primarily coke fines and is unsuitable for sale. This sludge, approximately 45 tons per month, is separated and requires disposal.

Many different options were examined in an effort to most efficiently dispose of these wastes. The utilization of the tar sludge as a roofing material and in asphalt mixes was studied. Also, experiments are being conducted in an effort to recycle the waste oil back to the rolling mills. The most promising method of disposal, however, appeared to be recycling the oils and tars to either the blast furnace or coke ovens. Bench scale mixes were made of these sludges with a variety of materials including limestone, slag, blast furnace dry dust, flue dust, coal and coke breeze. The optimum mix, chosen on the basis of mixing, handleability and ease of disposal, was 7:1 mixture of coal and sludge to be charged into the coke ovens. Pilot testing was carried out using a Simpson Muller mixer. It was concluded that the Muller mixer was a satisfactory piece of equipment for this application and work proceeded on a full-scale installation.

The mixing operation was set up at the #1 Coke Plant Coal Handling and is operated by coke plant personnel. A Simpson Muller mixer, size number 3, was installed (see Figure 1). The mixer consists of an 8' diameter circular pan 36" deep with a capacity of 25-30 feet^3. Two large Mullers or wheels sit vertically inside the pan hinged to a central vertical shaft by rocker arms. These wheels are 36" in diameter, 11" wide, and weigh 2200 lbs. each. The Mullers rotate horizontally around the central vertical shaft at 19½ RPM. In addition to the horizontal rotation in the pan, each Muller is free to rotate on its own axle. The unit is powered by a 40 HP-1200 RPM motor. Adjustment of set screws maintains the Mullers from 1/8" to 2" above the bottom of the pan, depending on the nature of the process and the materials to be mixed. The purpose of this arrangement is to provide mulling rather than grinding and to mix rather than pulverize. Plows located both inside and outside of the mullers serve two functions. The first is to turn the material over and place it in front of the Mullers for the twist and squeeze of the mulling action. The second, after the mulling, the bottom discharge door is opened and the plows automatically clear the mixer.

The mixing of the tar and oily sludges is a batch process. The sludges are collected from throughout the plant and stored in a containment bin located near the mixer. A front-end loader places the coal and sludge into the mixer from the top. A high-volatile coal is used in the mix since it is not as critical a component in the coal mix required for the ovens as low-volatile coal. A batch consists of 3,000 pounds of which 450 pounds, 15%, is tar and oily sludge. After a mixing time of 15 minutes, the mixture is bottom-dumped onto a conveyor and transferred to a stockpile. The total batch time is 30 minutes (see Figure 2). The unit has the capacity to process over 10 tons of sludge per day, yielding 72 tons of coal-sludge mix. The unit is currently handling 9.3 tons of sludge per day, five days per week, and generating 62 tons of coal-sludge mix per day. The addition of the sludge and the mixing action increases the bulk density of the mix to 65 lbs/ft^3. The coal-sludge mix, therefore, is blended with other coals before charging into the ovens. This further dilutes the mix by a factor of 145. The ultimate coal-to-sludge ratio is approximately 1,000 to 1. Because of this dilution, any contaminants present in the sludge such as iron or alkalis will not be significant. The coal-sludge mix does not cause equipment or processing problems in coal handling or charging.

Once in the coke ovens, a small portion of the tars and oils will be converted into coke. Most of the tar and oil will vaporize. The tar will be condensed and collected as the tar by-product. The vaporized oil will remain in the coke oven gas and contribute to its heating value.

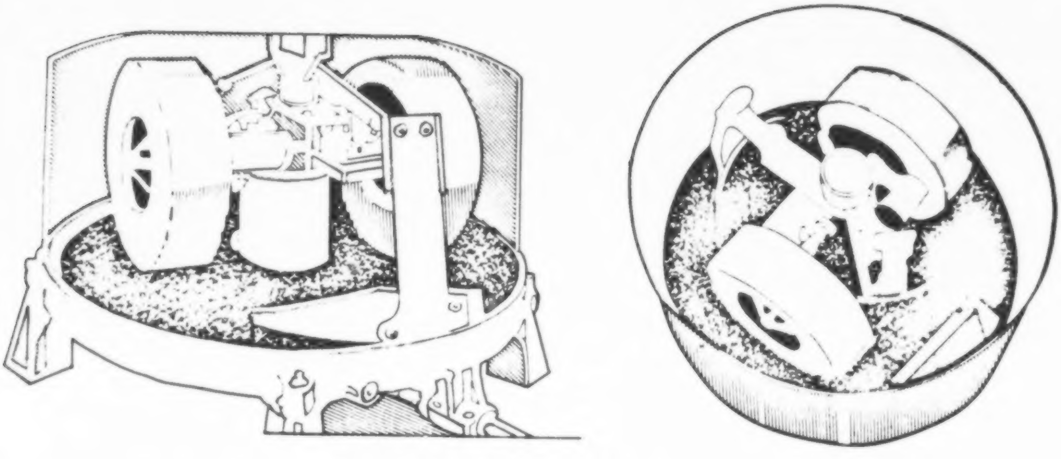

Figure 1. Muller Mixer

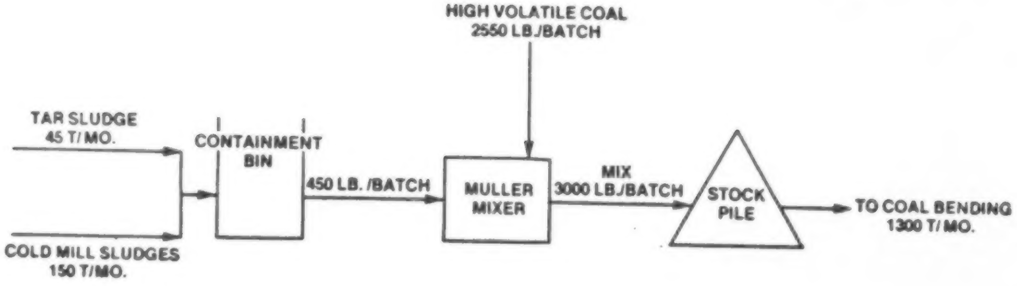
HIGH VOLATILE COAL
2550 LB./BATCH
TAR SLUDGE
45 T/MO.
CONTAINMENT
BIN
COLD MILL SLUDGES
150 T/MO.
450 LB. /BATCH
MULLER
MIXER
MIX
3000 LB./BATCH
STOCK
PILE
TO COAL BENDING
1300 T/MO.

Figure 2. Tar and Oily Sludge Disposal

APPENDIX

Attendees

Abbas	Syed Hasan	10143 Hartford Court #1B	Schiller Park	IL	60176	Northwestern University
Ackermann	Kurt J.	3426 E. 89th Street	Chicago	IL	60617	U.S. Steel Corporation
Adler	A.	100 King Street W.	Hamilton, Ontario	CANADA	L8N 3T1	Stelco Inc.
Allison	Earl L.	1650 45th Avenue	Munster	IN	46321	Andco Technical Services, Inc.
Alushin	Michael	401 M Street, S. W.	Washington	DC	20024	U.S. EPA
Amendola	Gary A.	25089 Center Ridge Road	Westlake	OH	44145	U.S. EPA, Region V
Antoine	Jacques	LECES B. P. 36	57210 Maizieres Metz	FRANCE		LECES
Aragian	Bill	P. O. Box 460, Burlington St.	Hamilton, Ontario	CANADA	L8N 3J5	DOFASCO Inc.
Armbrust	Robert A.	600 Delaware Avenue	Buffalo	NY	14202	NY State Dept. of Env. Conservation
Armour	Frank K.	135th Street and Perry Avenue	Chicago	IL	60627	Interlake, Inc.
Aronds	C. A.	P. O. Box 10000	1970 CA Ijmuiden	NETHERLANDS		Estel Hoogovens BV
Ashley	Dennis	P. O. Box 1101	Jackson	MI	49204	MacSteel Div./Quanex Corp.
Ayer	Franklin A.	P. O. Box 12194	Research Triangle Park	NC	27709	Research Triangle Institute
Bakk	Dan	230 South Dearborn Street (5EAE)	Chicago	IL	60604	U.S. EPA, Region V
Balajee	Shank R.	3001 East Columbus Drive	East Chicago	IN	46312	Inland Steel Company
Banker	Lalit	4505 Creedmoor Road	Raleigh	NC	27612	Midwest Research Institute
Barkdoll	Michael P.	P. O. Box 2511	Knoxville	TN	37901	Enviro-Measure, Inc.
Barnes	Thomas M.	P. O. Box 1071	Butler	PA	16001	Heckett
Baskerville	Jesse	345 Courtland Street, N. E.	Atlanta	GA	30365	U.S. EPA
Beam	K.	Solandt Road	Kanata, Ontario	CANADA	K2K 2A5	Betz Inc.
Becker	Brooks	1406 E. Washington Avenue, Suite 124	Madison	WI	53703	Residuals Management Technology
Bedick	Robert C.	2400 Ardmore Boulevard	Pittsburgh	PA	15221	Energy Impact Associates
Benbenek	Jeff	115A West Main Street	Collinsville	IL	62234	Illinois EPA
Bhattacharyya	Aniruddha	Box A South Park Station	Buffalo	NY	14220	Donner-Hanna Coke Joint Venture
Bloom	Bernard	401 M Street, S. W.	Washington	DC	20460	U.S. EPA
Bodine	Pete	900 S. Mound	Attica	IN	47918	Harrison Steel Castings Co.
Branscome	Marvin R.	P. O. Box 12194	Research Triangle Park	NC	27709	Research Triangle Institute
Brantner	Karl A.	50 Staniford Street	Boston	MA	02114	Metcalf & Eddy, Inc.
Brookman	Edward T.	125 Silas Deane Highway	Wethersfield	CT	06109	TRC-Environmental Consultants, Inc.
Buchko	Nicholas S.	200 Neville Road	Pittsburgh	PA	15225	Shenango Incorporated
Caballero	Virgil	223 W. Jackson Boulevard	Chicago	IL	60606	Peter F. Loftus Corp.
Cason	Gary E.	600 Grant Street	Pittsburgh	PA	15230	U.S. Steel Corporation
Castonguay	Gilles C.	1220 Sheppard Avenue East	Willowdale, Ontario	CANADA	M2K 2T8	MacLaren Plansearch Inc.
Centi	Thomas J.	Park West II, Cliff Mine Road	Pittsburgh	PA	15275	NUS Corporation
Chadick	Bill	P. O. Box 96120	Houston	TX	77013	Armco Inc.
Cline, Jr.	Raymond A.	Weston Way	West Chester	PA	19380	Roy F. Weston, Inc.
Clouse	Bob	Butler Works	Butler	PA	16001	Armco Inc.
Cochran	Lynn	Highway 259 South	Lone Star	TX	75668	Lone Star Steel Co.
Cole	W. T.	100 King Street W.	Hamilton, Ontario	CANADA	L8N 3T1	Stelco Inc.
Cooper	Leah A.	Highway 259 South	Lone Star	TX	75668	Lone Star Steel Co.
Corkle	Bruce	223 W. Jackson Boulevard	Chicago	IL	60606	Peter F. Loftus Corp.
Cormier	Barbara L.	600 Grant Street	Pittsburgh	PA	15230	U.S. Steel Corporation
Cowherd, Jr.	Chatten	425 Volker Boulevard	Kansas City	MO	64110	Midwest Research Institute
Cox	Ian J.	2005 Walden Avenue	Buffalo	NY	14240	Andco Technical Services, Inc.
Coy	David W.	P. O. Box 12194	Research Triangle Park	NC	27709	Research Triangle Institute
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Dahlgren, Jr.	Allan G.	P. O. Box 401	Beaver Falls	PA	15010	Babcock & Wilcox Co.
Dale	Larry A.	One Erieview Plaza	Cleveland	OH	44114	The H. K. Ferguson Company
Dickerson	James H.	P. O. Box 59, MS 188	Gary	IN	46401	U.S. Steel Corporation, Gary Works
Dixon	Thomas E.	2970 U.S. Steel Building	Pittsburgh	PA	15219	Baumco Inc.
Downing	James M.	Route 33, McBride Lane	Knoxville	TN	37922	Mining Consultants, Inc.
Drapalik	Glenn C.	One Brown & Root Center	Lombard	IL	60148	Brown & Root, Inc.
Durrant	John	One Plymouth Meeting Mall	Plymouth Meeting	PA	19462	Betz-Converse Murdoch

Eastman	Douglas K.	1330 Burlington Street, E.	Hamilton, Ontario	CANADA	L8N 3J5	DOFASCO Inc.
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Elphinstone	David D.	600 Grant Street	Pittsburgh	PA	15230	U.S. Steel Corporation
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Erickson	Boyd C.	Geneva Works, P. O. Box 510	Provo	UT	84603	U.S. Steel Corporation
Fields	Stephen F.	7449 N. Natchez Avenue	Niles	IL	60648	Gard, Inc.
FitzPatrick	Joseph A.	The Technological Institute	Evanston	IL	60201	Northwestern University
Francis	Steven	1801 Crawford Street	Middletown	OH	45043	Armco Inc.
Fullerton	R. W.	125 Jamison Lane	Monroeville	PA	15146	U.S. Steel Corporation
Gatehouse, Jr.	Clifton M.	355 5th Avenue	Pittsburgh	PA	15222	Kaiser Engineers
Goldman	Leonard J.	P. O. Box 12194	Research Triangle Park	NC	27709	Research Triangle Institute
Goonan	Thomas G.	200 N. 7th Street	Lebanon	PA	17042	General Electric
Gredell	Eric	4800 E. 63rd Street	Kansas City	MO	64130	Burns & McDonnell Engineering Co.
Green	Howard T.	2727 Symmes Road	Hamilton	OH	45014	Steel Abrasives Inc.
Greene	Kevin	59 E. Van Buren	Chicago	IL	60605	Citizens for a Better Environment
Greenfield	Murray	P. O. Box 460	Hamilton, Ontario	CANADA	L8N 3J5	DOFASCO Inc.
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Hall	Stephen A.	50 Staniford Street	Boston	MA	02114	Metcalf & Eddy, Inc.
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Haney, Jr.	D. L.	174 S. 26th Street	Gadsden	AL	35901	Republic Steel Corp.
Hanson	Michael A.	208 S. La Salle Street	Chicago	IL	60005	U.S. Steel Corporation
Harrington	James T.	55 W. Monroe, Suite 1500	Chicago	IL	60603	Rooks, Pitts, Fullagar & Poust
Haskill	J.	13th Floor, PVM, EPS/WPCD	Ottawa, Ontario	CANADA	K1A 1C8	Government of Canada
Hawthorne	J. O.	125 Jamison Lane	Monroeville	PA	15146	U.S. Steel Corporation
Hendriks	Robert V.	IERL, MD-63	Research Triangle Park	NC	27711	U.S. EPA
Hepola	John	1201 Elm Street	Dallas	TX	75270	U.S. EPA
Hlustick	Dwight	401 M Street, S. W.	Washington	DC	20460	U.S. EPA
Hudiburgh	Gary	401 M Street, SW, Permits Div. EN-336	Washington	DC	20460	U.S. EPA
Hurt, Jr.	George	230 South Dearborn Street	Chicago	IL	60604	U.S. EPA, Region V
Jablin	Richard	2511 Woodrow Street	Durham	NC	27705	Richard Jablin & Associates
Johnson, Jr	John H.	345 Courtland Street	Atlanta	GA	30306	U.S. EPA
Johnston	Eileen L.	505 Maple Avenue	Wilmette	IL	60091	Illinois Waste Alert (IL EPA sponsored)
Kalinowsky	Roger	Tecumseh Road	Ecorse	MI	48229	Great Lakes Steel
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Kemner	William F.	11499 Chester Road	Cincinnati	OH	45246	PEDCo Environmental Inc.
Kesari	Laxmi N.	401 M Street, S. W.	Washington	DC	20460	U.S. EPA
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Kirshner	Marvin	2400 Ardmore Boulevard	Pittsburgh	PA	15221	Energy Impact Associates
Kleinvehn	L. A.	552 S. Washington Street	Naperville	IL	60566	Aquatechnics, Inc.
Koch	Robert	1801 Research Boulevard	Rockville	MD	20850	Geomet Technologies, Inc.
Kohlmann	Harold J.	1250 Broadway	New York	NY	10022	Hydrotechnic Corporation
Kovacevic	Radomir	1400 Hopkins Street	Whitby, Ontario	CANADA	L1N 2C3	Ferrco Engineering Ltd.
Krikau	Fred G.	135th Street and Perry Avenue	Chicago	IL	60627	Interlake, Inc.
Krishnakumar	C. K.	7449 N. Natchez Avenue	Niles	IL	60648	Gard, Inc.
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Lang	D. C.	3210 Watling Street	East Chicago	IN	46312	Inland Steel Company
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Lawrence	Robert	19 Pebble Road	Newtown	CT	06470	KPN Associates
Levine	Sy	1701 First Avenue	Maywood	IL	60153	Illinois EPA
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Litman	Craig A.	215 Fremont Street	San Francisco	CA	94105	U.S. EPA, Region X
Littlewood	Roy	100 King Street W.	Hamilton, Ontario	CANADA	L8N 3T1	Stelco Inc.
Luton	John	P. O. Box 96120	Houston	TX	77013	Armco Inc.
MacDowell	William L.	230 South Dearborn Street (5EAE)	Chicago	IL	60604	U.S. EPA, Region V
Margolin	Stanley V.	Acorn Park	Cambridge	MA	02140	Arthur D. Little, Inc.
Masciantonio	Philip X.	600 Grant Street (Room 1876)	Pittsburgh	PA	15230	U.S. Steel Corporation
Maslany	Thomas J.	6th and Walnut Streets, Curtis Bldg.	Philadelphia	PA	19106	U.S. EPA, Region III
Mastey	Tony	1221 Avenue of the Americas	New York	NY	10020	33 Metal Producing Magazine
Matuschkovitz	Richard	230 South Dearborn Street	Chicago	IL	60604	U.S. EPA, Region V
Matuza	Ray	7603 Sugarbush Trail	Hudson	OH	44236	Betz Laboratories
Mauck	Michael O.	P. O. Box 59, MS 188	Gary	IN	46401	U.S. Steel Corporation, Gary Works
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McMullen	Robert M.	Martin Tower	Bethlehem	PA	18016	Bethlehem Steel Corporation
Mears	Connally E.	1860 Lincoln Street	Denver	CO	80295	U.S. EPA, Region VIII
Melcer	Henryk	P. O. Box 5050, Wastewater Tech. Ctr.	Burlington, Ontario	CANADA	L7R 4A6	Environmental Protection Service
Mendelson	J. T.	8th and Eaton Avenues	Bethlehem	PA	18016	Bethlehem Steel Corporation
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Milhau	Alain	14, Bd. du General Leclerc	92522 Neuilly Sur Seine	FRANCE		Ministere de l'Environnement
Miller	Bruce	345 Courtland Street, N. W.	Atlanta	GA	30308	U.S. EPA
Miner	Robert P.	200 N. 7th Street	Lebanon	PA	17042	General Electric
Molnar	James A.	3001 Miller Road	Dearborn	MI	48126	Ford Motor Company
Morris	Arthur E.	Dept. of Metallurgical Engineering	Rolla	MO	65401	University of Missouri-Rolla
Murray	Douglas T.	1500 Market Street	Philadelphia	PA	19101	ARCO Performance Chemicals Co.
Nemeth	Richard L.	3100 East 45th Street	Cleveland	OH	44127	Republic Steel Corp.
Neveril	Robert B.	7449 N. Natchez Avenue	Niles	IL	60648	Gard, Inc.
Nicola	A. B.	32nd and Avery	Pittsburgh	PA	15201	Pennsylvania Engineering Corp.
Norlund	Victor V.	P. O. Box 59, MS 188	Gary	IN	46401	U.S. Steel Corporation, Gary Works
Oda	Terry N.	6th and Walnut Streets	Philadelphia	PA	19106	U.S. EPA, Region III
O'Donnell	William R.	227 S. Division Street	Zelienople	PA	16063	Sybron/Leopold
O'Keefe	Thomas J.	Dept. of Metallurgical Engineering	Rolla	MO	65401	University of Missouri-Rolla
Olthof	M.	3185 Babcock Boulevard	Pittsburgh	PA	15237	Duncan, Lagnese & Associates
Oppelt	E. Timothy	26 West St. Clair	Cincinnati	OH	45268	U.S. EPA
Ostrov	Richard	401 M Street, S. W.	Washington	DC	20460	U.S. EPA
Paquette	Steven	Parkwest II, Cliff Mine Road	Pittsburgh	PA	15275	NUS Corporation
Parikh	Dilip	10 Chatham Road	Summit	NJ	07901	MikroPul Corporation
Patton	James D.	10 Chatham Road	Summit	NJ	07901	MikroPul Corporation
Pekron	Phil	230 South Dearborn Street (5EAE)	Chicago	IL	60604	U.S. EPA, Region V
Peterson	Joseph	515 S. Harmon Street	Indianapolis	IN	46206	Crown Environmental Control
Piper	Steve	213 Burlington Road	Bedford	MA	01730	GCA/Technology Division
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Radigan	Patrick K.	2800 Grant Building	Pittsburgh	PA	15219	National Steel Corp.
Randolph	Lonnie	20545 Center Ridge Road	Cleveland	OH	44116	American Cyanamid Co.
Rasmussen	Stig	9165 Rumsey Road	Columbia	MD	21044	Niro Atomizer Inc.
Ratajczyk	John W.	1901 South Prairie Avenue	Waukesha	WI	53186	Envirex Inc.
Reetz	Helen	3210 Watling Street	East Chicago	IN	46312	Inland Steel Company
Reeverts	David	P. O. Box 1101	Jackson	MI	49204	MacSteel Div./Quanex Corp.
Reggi	John	1911 Warwood Avenue	Wheeling	WV	26003	West Virginia APC Commission

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Rolfe	Kevin	P. O. Box 8944	Auckland 1	NEW ZEALAND		Department of Health
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Schlosser	Robert W.	550 Pinetown Road	Fort Washington	PA	19034	JACA Corp.
Schreibeis	Lee J.	Room 1636 Martin Tower	Bethlehem	PA	18016	Bethlehem Steel Corporation
Schwartz	Stephen M.	1000 16th Street, N. W.	Washington	DC	20036	American Iron and Steel Institute
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Skelding	Thomas L.	P. O. Box 1101	Jackson	MI	49204	MacSteel Div./Quanex Corp.
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Staley	Jeff	3210 Watling Street	East Chicago	IN	46312	Inland Steel Company
Stasiak	Edward B.	3426 E. 89th Street	Chicago	IL	60617	U.S. Steel Corp.
Steiner	Bruce A.	P. O. Box 600	Middletown	OH	45043	Armco Inc.
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Styple	Ken	119 Littleton Road	Parsippany	NJ	07054	Enviro-Systems/Belco
Suitlas	John R.	Three Springs Drive	Weirton	WV	26062	National Steel Research and Development
Szuhay	Lawrence A.	P. O. Box 6778	Cleveland	OH	44127	Republic Steel Corp.
Szwed	Daniel F.	Box 832, Butler Works	Butler	PA	16001	Armco Inc.
Tarbert	Richard E.	125 Jamison Lane	Monroeville	PA	15146	U.S. Steel Corporation
Telford	Tony	2200 Churchill Road	Springfield	IL	62706	Illinois EPA
Terril	Mark E.	125 Jamison Lane	Monroeville	PA	15146	U.S. Steel Corporation
Thomas	Michael J.	11600 S. Burley Avenue	Chicago	IL	60617	Republic Steel Corp.
Tower	Kevin C.	125 Silas Deane Highway	Wethersfield	CT	06118	TRC-Environmental Consultants, Inc.
Trontell	Christine S.	P. O. Box 316	Pueblo	CO	81002	CF&I Steel Corporation
Tucker	Thomas	P. O. Box 59, MS 188	Gary	IN	46401	U.S. Steel Corporation, Gary Works
Tucker	William B.	P. O. Box 6778	Cleveland	OH	44127	Republic Steel Corp.
Tuckerman	Robert	One Erieview Plaza	Cleveland	OH	44114	The H. K. Ferguson Company
Turnage	J. W.	125 Jamison Lane	Monroeville	PA	15146	U.S. Steel Corporation
Udovich	William J.	11600 S. Burley Avenue	Chicago	IL	60617	Republic Steel Corp.
Umene	Eiji	12/14 Avenue Hamoir	1180 Brussels	BELGIUM		International Iron and Steel Institute
Vajda	Frank A.	Koppers Building	Pittsburgh	PA	15219	Koppers Company, Inc.
Vajda	Stephen	900 Agnew Road	Pittsburgh	PA	15227	Jones & Laughlin Steel Corp.
Vakharia	Nik	P. O. Box 6778, 800R	Cleveland	OH	44101	Republic Steel Corp.
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Verbosky	G.	Eng'g Dept.-800R, P. O. Box 6778	Cleveland	OH	44101	Republic Steel Corp.
Villalobos	Mel	1701 First Avenue	Maywood	IL	60153	Illinois EPA
Vogt	John	140 Centennial Parkway N.	Stoney Creek, Ontario	CANADA	L8E 3H2	Environment Ontario
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Wallace	Anna W.	P. O. Box 12194	Research Triangle Park	NC	27709	Research Triangle Institute
Wallace	Dennis D.	425 Volker Boulevard	Kansas City	MO	64110	Midwest Research Institute
Wallace, Jr.	James T.	P. O. Box 5200	Cherry Hill	NJ	08034	Stone & Webster Engineering Corp.
Walsh	Joe P.		Sharon	PA	16144	Sharon Steel Corp.
Wanker	L. David	20545 Center Ridge Road	Cleveland	OH	44116	American Cyanamid Co.

Watson	Robert G.	2901 Butterfield Road	Oak Brook	IL	60523	Nalco Chemical Co.
Whitehead	Martin	628 W. Parklane Towers	Dearborn	MI	48126	Ford Motor Company
Wilhelmi	A. R.		Rothschild	WI	54474	Zimpro Inc.
Wilson, Jr.	Leon W.	Research Laboratory, MS 54	Monroeville	PA	15146	U.S. Steel Corporation
Wise	Steve	1400 S. Route 31	McHenry	IL	60050	Lodge-Cottrell
Wisniewski	Leonard D.	3100 East 45th Street	Cleveland	OH	44127	Republic Steel Corp.
Withrow	Bill	309 W. Washington	Chicago	IL	60606	Illinois Pollution Control Board
Wojciechowski	Edward	230 South Dearborn Street (5EAE)	Chicago	IL	60604	U.S. EPA, Region V
Wong-Chong	George M.	601 Grant Street, 10th Floor	Pittsburgh	PA	15219	Environmental Research & Technology Inc.
Workman	W. S.	125 Jamison Lane	Monroeville	PA	15146	U.S. Steel Corporation
Yamaguchi	I.	10400 W. Higgins	Rosemont	IL	60018	Okura & Co.
Young, Jr.	Earle F.	1000 16th Street, N. W.	Washington	DC	20036	American Iron and Steel Institute
Zavoda	Rich	6801 Brecksville Road	Independence	OH	44131	Republic Steel Research Center
Zwikl	James R.	200 Neville Road	Pittsburgh	PA	15225	Shenango Incorporated

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